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(54) METHOD FOR SEPAI



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(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a material suitable for removing water from oil contaminated with water and in particular to a material suitable for removing traces of water from petroleum products.

15 In the refining of petroleum products, particularly middle distillates, the products are frequently submitted to a stream stripping operation to remove light ends and other contaminants. Occasionally traces of moisture are left behind in the product in the form of a dilute water-in-oil emulsion which gives the product an undesirable hazy appearance. Such emulsions can be difficult to break.

20 Similar emulsions can also be formed as a result of storage. In storage tanks oil absorbs water which eventually separates as a layer on the bottom. When product is pumped out the resulting disturbance disperses the water throughout the oil producing an unsightly hazy dispersion.

25 These emulsions can give rise to corrosion problems caused by the precipitation of water from wet products. There is a particular need for water removal from aviation kerosine since its presence would cause operational difficulties.

30 Sand filters are used to remove traces of water from oil by coalescence (and vice versa) but to date they have not been found capable of consistently removing haze. Salt filters can also be used but these can lead to excessive corrosion downstream.

35 We have now discovered that treating sand and similar coalescing media with certain polymers improves their coalescing power and enables them to remove haze from middle distillates.

40 Thus according to the present invention there is provided a method for separating

with water
a contam-
ination bed

containing solid particles treated by contacting the solids with an aqueous solution of a water soluble polymer containing cations which are adsorbed on to the surface of the particulate material, in such manner that the water coalesces, an oil phase and a water phase are formed and a substantially water-free oil is recovered.

Suitable polymers include medium to high molecular weight polyamides and polyacrylamides.

The terms "medium" and "high" molecular weights relate to values in the order of $0.5-1.0 \times 10^6$ and $10-12 \times 10^6$ respectively.

The preferred polymer is a high molecular weight polyacrylamide.

Suitable particulate solids include such materials as anthracite, charcoal, polystyrene, polyethylene, polypropylene, vermiculite and glass beads. The preferred solid is itself basically hydrophilic rather than hydrophobic and should contain suitable adsorption sites on its surface. Example of such materials are river gravel and sand.

The solids may be contacted with the polymer solution by soaking in it or by passing the solution through the bed of particles prior to use.

At low flow rates there is little advantage to be gained in using the improved material of the present invention. The difference between treated and untreated material becomes more marked with higher flow rates, e.g., hydraulic loading of at least $2 \text{ m}^3/\text{m}^2/\text{hr}$.

Preferred hydraulic loadings are in the range $4-10 \text{ m}^3/\text{m}^2/\text{hr}$.

Petroleum distillates having a hazy appearance due to water are suitable feedstocks, particularly gas oils.

After lengthy use the efficiency of the purification bed may deteriorate. It may be regenerated by treating it again with the water soluble polymer in a similar fashion.

The invention is illustrated by the following examples.

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Example 1

200 gm of river sands were added to 750 ml of a 50 ppm solution of Magnafloc 140 in distilled water, contained in a flask and
 5 rotated for ~16 hours in an end-over-end shaker.

The sand was filtered from the liquid and dried in an oven at 50°C.

10 Simulated hazy gas oil containing about 500—550 ppm water was produced by mixing in a Vortex mixer for 20 seconds in quantities of 500 ml. The resultant hazy gas oil will remain stable for long periods of time.

15 Hazy gas oil was pumped at 500 ml/hr in downward flow through a column 13 cm long X 1.2 cm diameter containing 20 gm of treated sand which had been saturated in situ with distilled water.

20 The void volume of bed was 5 ml.

Filtered gas oil remained clear for 7 hours, i.e., 700 bed volumes.

In a parallel experiment, using untreated sand, the gas oil emerged hazy immediately.

25 Magnafloc 140 is a polyacrylamide supplied by Allied Colloids Limited.

Example 2

30 A solution of Zetag 76 was prepared in the laboratory by dissolving 0.5 of Zetag 76 in 3 ml of methanol, followed by 97 ml of water, (Solution A).

Two 20 gm beds of river sand were prepared using a mixture of 10 gm >30 mesh sand in the bottom of a tube similar to that
 35 used in Example 1 with 10 gm of 30—44 mesh sand packed into the top of the tube.

The first bed (Column A) was left standing overnight in 100 ml of distilled water.

40 The second bed (Column B) was left overnight in 10 ml of Solution A which had been shaken with 90 ml of distilled water.

45 Simulated hazy gas oil containing 600 ppm water was produced by mixing in an Atomix mixer was 60 seconds on maximum speed. The resultant hazy gas oil will remain stable for long periods of time.

50 Hazy gas oil was pumped through the beds at 500 ml/hr in a downward flow. Initially the gas oil from Column A was hazy while

the gas oil from Column B was almost clear. After 7 hours the untreated bed produced slightly hazy gas oil while the treated bed gave a clear gas oil.

Zetag 76 is a water soluble cationic poly-electrolyte supplied by Allied Colloids Limited. 55

WHAT WE CLAIM IS:—

1. A method for separating water from 60 oil contaminated with water which method comprises passing a contaminated oil stream through a purification bed containing solid particles treated by contacting the solids with an aqueous solution of a water-soluble 65 polymer containing cations which are adsorbed on to the surface of the particulate solids, in such manner that the water coalesces, an oil phase and a water phase are formed, and a substantially water-free oil 70 is recovered.

2. A method according to Claim 1 wherein the polymer is a high molecular weight polyacrylamide.

3. A method according to either of the 75 preceding claims wherein the solids are hydrophilic.

4. A method according to Claim 3 wherein the solids are gravel or sand.

5. A method according to any of the 80 preceding claims wherein the hydraulic loading of the stream with respect to the purification of the bed is at least 2 m²/m³/hr.

6. A method according to Claim 5 wherein the hydraulic loading is in the range 85 4—10 m³m²/hr.

7. A method according to any of the preceding claims wherein the feedstock is a gas oil having a hazy appearance due to 90 water and a clear gas oil is recovered.

8. A method for the clarification of hazy gas oil as hereinbefore described with reference to the Examples.

9. Products whenever prepared by a 95 process according to any of the preceding claims.

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 Agent for the Applicants.



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<p>(21) International Application Number: PCT/US92/03428</p> <p>(22) International Filing Date: 24 April 1992 (24.04.92)</p> <p>(71) Applicant (for all designated States except US): HYDRA-TECH HYDRAULICS, INC. [US/US]; 24724 South Wilmington Avenue, Carson, CA 90745 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only) : CULBERT, Robert, M. [US/US]; 713 33rd Street, Manhattan Beach, CA 90266 (US). PARKER, Steven, C. [US/US]; 22792 Via Santa Rosa, Mission Viejo, CA 92691 (US).</p> <p>(74) Agent: CARNEY, Hayden, A.; P.O. Box 7068, Pasadena, CA 91109-7068 (US).</p>		<p>(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: EXTRACTION OF WATER FROM OIL</p> <div data-bbox="630 1142 1073 1682"> </div> <p>(57) Abstract</p> <p>A bag type device (2) for extracting water from oil includes a bag (3) with an outer layer of felt (20) lined by at least one layer (22) of water absorbing laminate. The interior of the bag is composed of a plurality of slit sheets of water absorbing laminate forming a plurality of finger-like strips (35) depending from adjacent the top of the bag. The strips are preferably longer than the length of the bag. The bag and the water-absorbing layers within the bag are supported by a wire ring (30) stitched into a hem around the open upper end of the bag. As oil is passed through the bag, the finger-like strips provide an increased surface area for absorption of water from the oil. The strips can expand inwardly and toward the oil flow to prevent back-pressure build up within the bag.</p>		

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EXTRACTION OF WATER FROM OIL**Field of the Invention**

The invention relates generally to a filter, and more specifically, to a bag-type water absorbing element for extracting water from oil.

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Background of the Invention

A machine requires oil to lubricate the various moving parts within the machine. Without proper lubrication, the machine may not perform properly and may prematurely wear. This can lead to a shorter life span for the machine and increased maintenance costs. When a foreign fluid, such as water, enters the oil, the lubricity and other properties of the oil may be detrimentally affected. Manufacturers may not warrant a machine if too much residual water is present in the lubricating oil. It is, therefore, important to keep the machine properly lubricated with oil which is free of or contains only very low levels of water.

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It is not always possible, however, to keep the oil dry. Machines, such as can seamers used in the brewing and canning industries, are routinely hosed down and steam-cleaned. These machines are also often subjected to changing temperatures which can cause moisture to accumulate on or within the machine. Water may leak into the interior components of the machine and enter the oil supply.

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In addition to adversely affecting the lubricity of the oil, as little as 1% residual water in the oil may cause several other problems. Even within an oil environment, water can lead to rust which severely impairs precision parts such as gear mechanisms and bearings. Moreover, the water may lead to hydrogen embrittlement of metal which causes metal particulates to break away and cracks to form. The particulates

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1 may act as abrasive grains in the machine and limit its performance. Furthermore,
water molecules can enter the cracks and form additional rust centers within parts of
the machine.

5 When specialized types of oil compounds having anti-wear and other additives are
used to lubricate the machine, water dispersed in the oil can react with the zinc, e.g.,
used in many of such oils. The product of this reaction is a metal soap which can clog
valves and other precision machine components. Furthermore, the water oxidizes the
antifoam and stabilizer packages present in the oil which may reduce the viscosity of
10 the oil, and lead to friction wear between adjacent moving parts.

Due to the detrimental effects described, the lubricated machines will have to be
serviced more frequently, leading to undue system shutdown events and increased
costs. Many of these effects can be prevented by providing a system for extracting
dispersed water from the lubricating oil.

15 Various devices and methods have been proposed and employed to extract water
from oil, but each suffers from distinct disadvantages. One approach is to use a water
absorbing material suspended in a fiberglass mat in a pleated format much like an
automobile air or oil filter. The fiberglass mat is laminated in a construction in which
the fiberglass is spun-bonded between a propylene-base paper-like sheet and filter
20 paper.

This filter suffers from a large size, low water extraction capacity, and inability to
extract water from oils which retain water as a very fine dispersion of water in oil.
Also, as the oil viscosity increases, the performance of this type of filter drastically
decreases. If a water disperser is present in the oil, as is the case with many high
25 quality oils, this filter can only achieve an often-unacceptable 1% residual water level
in the oil. Due to its low capacity, the filter must be replaced frequently, leading to
overall system shutdown and increased maintenance costs. Due to the large size of the
filter, a large amount of usable oil is removed from the oil circulation system when the
filter is replaced. This oil must either be replaced or drip drained back into the
30 machine. Each choice is time consuming and potentially costly. Costs are especially
great for replacing used filters because used oil is classified as a toxic substance which
must be disposed of in a specified and costly manner.

35 Recently, bag-type water extractors have been introduced to provide an alternative
to the fiberglass laminate filters. These bag-type filters have a bag-shaped exterior and
several layers of water absorbing laminate lining the interior of the bag. Wet oil is

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1 passed through an opening at the top of the bag and through the lining which extracts
the water from the oil. Although this type of filter is smaller than the pleated
fiberglass filter and takes a substantially lower amount of usable oil from the system
5 when the filter is replaced, the bag suffers from an easy flow path for the oil to pass
directly to the bottom of the bag. The lining on the sides of the bag can be bypassed.
If an increased amount of water absorbing material is used within the bag, the bag
suffers from an unacceptable back pressure which may strain the recirculating pump
which moves oil from the machine through the extractor. That back pressure is
10 produced because the water absorbing material swells and expands as it absorbs water
from the oil, and that expansion closes off the passages in the filter through which the
oil must flow to exit from the filter.

In light of the foregoing, a need exists for an improved filter element for
extracting dispersed water from oil and other non-aqueous liquids and in which the
15 element has one or more of the following characteristics: low retained oil volume,
high water sorption capacity, useful with high viscosity liquids, useful in existing
water-removal liquid handling systems, does not manifest high back pressure before
replacement of the element is timely in terms of sorption capacity or sorption
efficiency, compatible with additives in high-performance lubricants, produces low
20 residual water levels in the filtrate, and cost effective in comparison to existing water
extraction devices.

Summary of the Invention

25 This invention addresses the need identified above. It does so by providing a
structurally simple and readily made bag-type filter element which efficiently and
effectively removes dispersed water from oil, e.g.

Generally, the present invention provides a bag-type water extraction element
including a bag having a closed bottom and an open top, a bag support near the top of
30 the bag, and at least one layer of water sorbing material essentially fully covering the
inner surface of the bag. The water sorbing material is provided in the form of a
plurality of filaments which depend into the bag from adjacent the bag top.

To facilitate the needs of users, the diameter and length of the bag can be varied
to allow the bag to fit various containers. The filaments of water sorbing material
35 produce a low volume, high capacity extractor element which does not have to be

1 frequently replaced. These desirable characteristics are retained even in the presence of viscous, high-grade oils.

As used herein, the term sorbtion includes both absorbtion, in which water is taken into and retained in the sorbtion medium, and absorbtion in which water
5 molecules and droplets are held on the surface of the sorbtion medium.

Brief Description of the Drawings

The above-mentioned and other features of the present invention are more fully set forth in the following description of the presently preferred and other embodiments of a bag-type water extractor, which description is presented with reference to the
10 accompanying drawings in which:

FIG. 1 is a schematic diagram of a lubricating oil recirculating system for a machine;

15 FIG. 2 is an elevation view, partially in cross-section, of an extractor according to the present invention;

FIG. 3 is a cross-sectional elevation view of a portion of the extractor and of a canister assembly for housing the extractor;

20 FIG. 4 is a simplified cross-sectional view of the extractor;

FIG. 5 is a plan view of the outer layer of the extractor ready for forming into finished form;

FIG. 6 is a plan view of a lining sheet used within the extractor ready for forming into finished form;

25 FIG. 7 is a plan view of a slit absorber sheet used as part of the interior filament assembly of the extractor;

FIG. 8 is a perspective view of a subassembly of the sheets shown in FIG. 7;

FIG. 9 is a perspective view of a portion of the extractor showing the several layers of the bag-type extractor;

30 FIG. 10 is a cross-sectional elevation view of a portion of the extractor showing the wire ring and bias canvas for providing support for the bag; and

FIG. 11 is an elevation view showing the bias canvas folded over the wire ring to complete assembly of the support of FIG. 10.

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1 **Detailed Description of the Invention**

 Referring to FIG. 1, an oil recirculating system for removing water and
 particulates from lubricating oil includes a lubricated machine 4 from which oil is
 pumped through a suitable pump 6. The machine may be a can seamer, for example,
5 commonly used in the brewing industry or any other machine requiring substantially
 water-free oil for effective lubrication of the machine. The pump circulates the oil
 from the machine into a water extraction unit 1 which removes at least some of the
 water from the oil. Downstream from the extractor, a filter 8 removes particulates
10 from the oil. After numerous circulations through the system, the oil becomes
 essentially dry and particle-free, and is reused in the machine.

 The water which is present in the oil in machine 4 commonly is in a colloidal
 dispersion in the oil. The water is immiscible in the oil, and so is present in the oil
 as very fine droplets, perhaps even molecules, which are suspended in the oil.

15 Referring to FIG. 2, a water extractor 2 according to the present invention
 preferably includes a bag 3 having a closed bottom and an open top. The bag is
 preferably formed of a back-up fabric which, in a presently preferred extractor, is 50
 micron needled felt 20. The interior of the bag is lined with two unslit layers 22, 24
20 of high loft water sorbing material. One or more layers of high loft water sorbing
 filament 26, made of the same water sorbing material as the bag liner, are contained
 within the bag. The water sorbing material is preferably a superabsorbing polyacrylate
 polymer formed into a laminated sheet material such as Gelok 9503, a product of
 Gelok International Corp. of Dunbridge, Ohio. The presently preferred polymer is
25 polymer IM-1000 obtainable from Hoechst/Celanese Corp. A bag support ring 30 (see
 FIG. 3), preferably formed of wire, proximate the top of the bag serves as a support
 for the extractor during use of the extractor. Each of the layers of water sorbing
 filament 26 in the bag depend from adjacent the wire ring in a way broadly reminiscent
 of a hula skirt. The wire ring is enclosed in a hem formed by a strip of bias canvas
30 28 which is folded over the wire ring and stitched to each of the layers of the bag. A
 fabric strip handle 32 is stitched to the bias canvas for convenient handling of the
 extractor.

 Referring to FIG. 3, the extractor 2 is mounted within a conventional canister
 assembly 10 commonly used to house bag-type absorber elements used in lubricating
35 oil recirculating systems, e.g.. The container assembly includes a tank-like hollow
 container body 11 for holding the extractor. The wire support ring 30 of the extractor

1 rests upon an upward facing ledge 21 within the container body. The diameter of wire
ring 30 is sized to conform to conventional sizing standards for filter canisters and fits
conveniently on the ledge above a perforated metal basket 18 which depends from the
ledge within canister body 11. An annular side channel 23 is formed between the
5 basket and an inner wall 25 of the container body to allow oil to flow outwardly of the
basket. A removable lid 12 is held lightly on the body 11 via a clam shell cover clamp
13 which is composed of a pair of essentially c-shaped members 15 which are hinged
together (not shown) at one pair of adjacent ends and which are capable of being drawn
together over the lid and body rims by a conventional over-center toggle clamp
10 mechanism (not shown) engaged between the unhinged ends of the members. An
O-ring 17 is lodged between the container lid and body. The O-ring prevents leakage
from the closed canister of oil which is pumped at a selected pressure through the
water extraction assembly.

15 Recirculating oil enters the container assembly through an oil inlet 14 in the
container lid 12. As oil passes through the bag-type extractor, the water dispersed
within the oil is absorbed by the filaments 26 of sorbing material within the bag. The
filaments are composed of finger-like strips 35 which expand substantially inwardly of
20 basket 18 as they absorb water from oil flowing through the extractor. After passing
through the absorber filament array, the oil then passes through the unslit layers 22 of
sorbing material and the felt 20 which forms the outer portions of the extractor. The
oil then passes out of the extractor to the side channels 23 outside the perforated
basket, and through the bottom of the basket. The oil then passes out of the canister
25 assembly through oil outlet 16. The oil is then circulated to the particulate filter 8
(FIG. 1) where particulates are extracted from the oil.

As the oil passes through the unslit layers 22, 24 of water sorbing material,
some of the water dispersed in the oil is taken up by those layers, which then expand.
Those layers, however, define a liner in the outer felt bag and are forced, with the felt
30 bag itself, by the oil pressure in the bag against the inner surfaces of the perforated
basket which confines the bag. Expansion of sorbtion layers 22, 24, as they remove
water from the oil flowing through them, gradually constricts the liquid flow pores in
those layers, thereby increasing the resistance of the extractor to the flow of oil through
it. That flow resistance increase causes the back pressure in the extractor (i.e., the
35 pressure drops across the extractor) to rise. The resulting pressure drop across the
extractor can be readily monitored by pressure gages (not shown). When the extractor

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pressure drop increases, for example, from 20 psi to 25 psi, the extractor bag may need to be replaced.

Referring to FIG. 4, the interior filaments 26 of the bag preferably are composed of five slit sheets of superabsorbing laminate 35a-35e. As described more fully below, each slit sheet of laminate material is folded once on itself so that, in the presently preferred extractor, there are ten layers of water sorbing filaments about the inner circumference of the extractor bag. The finger-like strips (filaments) formed by the slit layers of laminate preferably have a length about 25% longer than the length of the bag. This allows absorption of water to occur at the bottom of the bag as well as along the sides. The strips are preferably intermingled at their ends 38 in such a way that the oil passing through the bag has no straight flow path through the extractor. However, the strips are free to move within the bag.

Referring to FIG. 5, the felt for bag 20 is cut according to the dimensions of the bag. The corners of the felt bag preferably are cut diagonally so the bag can fit snugly within the rounded perforated basket of the canister assembly. Referring to FIG. 6, each unslit sheet of water sorbtion material can be folded on itself to define the water sorbing liner (layers 22, 24) for the felt bag.

Referring to FIG. 7, the inner slit layers of sorbtion material have parallel slits traversing the entire sheet of laminate except for two end margins 40, 42, one on each end of the sheet. The sheets are die cut by a rule die converter, for example, to form slits 44 preferably along the machine direction of the sheet. The ends of the slits are inwardly of the end margins 40, 42 of the sheet.

Each slit sheet is then folded, as shown in FIG. 8, to cause the unslit end margins to register, thereby defining the equivalent of two smaller sheets slit from adjacent one end through the opposite end. This results in a stronger hula-skirt like configuration in the finished product. In a preferred embodiment, five sheets of water sorbing material are constructed in this manner.

The five separate folded sheets of slit superabsorber sheet are then stacked together, each adjacent slit sheet being offset from the neighboring sheet along the sheet end margins by an odd number of half widths of a strip formed between adjacent slits 44. In this way, the finger-like strips are free to intermingle and move between the strips of the adjacent sheet providing no straight flow path for the oil through the extractor. The five folded slit layers of water absorbing material preferably are stitched together along their registered end margins to produce a subassembly.

1 Referring to FIG. 9, the bias collar material 28, made of canvas or the like,
is stitched around the periphery of the felt 20 and the inner liner 22 and 24. The slit
superabsorber subassembly (FIG. 8) is then rolled into a cylinder having a diameter
5 substantially similar to the inner diameter of the bag and is inserted into the lined felt
bag. That subassembly is then stitched in place. Referring to FIG. 10, the bias collar
is then folded up and an appropriately sized wire ring 30 is inserted into the interior
to the folded collar. Referring to FIG. 11, the collar is then folded inside the bag and
the wire ring is secured by stitching the collar to entrap the ring in a hem. Additional
10 stitching can be provided at the lower end of the collar to secure the several layers of
the bag. Finally, the ends of the handle 32 are stitched to the collar beneath the wire
ring.

The described presently preferred embodiment of the invention provides several
advantages and addresses the needs described above. The filament-like strips of
15 sorbing material within the extractor provide high water sorbtion capacity. As the oil
flows through the bag, it follows a tortuous path through the finger-like strips of water
sorbing material within the bag. The maze of strips provides a low flow resistance
path. The length and circuitous nature of that path affords intimate contact between
the water dispersed in the oil and the sorbtion medium. There is a high effective
20 residence time of wet oil with the sorbtion medium per pass through the extractor.
There is also a very high effective sorbtion surface area produced by the strips because
both sides of the strips contact the oil.

The strips of sorbtion material are designed to be longer than the length of the
25 bag. The lower ends of the strips cover the bottom of the supporting bag to prevent
the oil from flowing preferentially through the bag bottom rather than through the
sorbtion material which lines the bag sides. The intermingled ends of the strips also
serve to maximize contact of the sorbtion medium with the water dispersed in the oil.

The unslit sorbtion material used as a lining in the outer support bag also
30 provides several advantages. First, the unslit material provides additional sorbtion for
the oil before it passes out of the bag. Second, using gauges already present on many
oil recirculating systems, the extractor provides a convenient method by which users
can determine when it is timely to replace the extractor bag with a fresh one. The
35 amount of unslit sorbtion material used in the bag liner is selected relative to the
quantity of filamented sorbtion material within the bag to provide a designed-in
pressure drop across the extractor when a selected portion of the water sorbtion

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1 capacity of the sorbtion medium has been used. That portion can be 100%, but
preferably is less than 100% and is a percentage which is empirically determined to
correspond to the optimum time to replace the extractor. That optimum time can be
5 determined in terms of a particular level of water extraction efficiency of the extractor,
or it can be in terms of a specified residual level of water-in-oil exiting the extractor,
for example. Furthermore, this pressure drop can readily be monitored by
conventional pressure gauges at the inlet and outlet ends of the container in which the
extractor is housed in use. If all of the sorbtion capacity of the extractor is provided
10 by filaments of sorbtion material in the bag, the pressure drop across the extractor
remains minimal throughout the sorbing life of the extractor. In that case, a user
would have to separately analyze (such as by use of the ASTM xylene extraction and
distillation method) the oil leaving the extractor for retained water content to know
when the water sorbtion capacity of the extractor has been consumed in full or in such
15 part as to warrant replacement of a spent extractor. On the other hand, if the sorbtion
capacity of an extractor according to this invention were provided entirely in the form
of unslit sorbtion medium along the inner walls of the bag, the extractor pressure drop
would grow to high levels long before the sorbtion capacity is consumed, the extractor
would have to be much larger, and the power of the oil circulation pump would have
20 to be greater. The present extractor combines low pressure drop and high useful
sorbton capacity in a small device which is useful with oil circulating pumps of modest
power rating.

The felt outer layer of the extractor bag also provides several advantages. The
25 felt acts as a support bag to house the relatively less strong and fragile sorbtion
material within the bag. As oil passes through the open end of the bag and through
and around the filaments, pieces of sorbtion strip material may break off and flow with
the oil. Also, the sorbtion medium, the super absorbing polymer, is present in
granular form in the sorbtion material laminate. Granules of the polymer can separate
30 from the laminate. The felt layer of the bag prevents these pieces of sorbtion material
and particles of sorbtion medium from exiting the extractor and therefore prevents
downstream valves and the like from becoming clogged. In addition, the felt acts as
a coarse particulate filter to extend the useful life of the downstream fine particulate
filter typically used in an oil recirculating systems.

35 Because of its inherent low resistance to liquid flow through it, the extractor
is able to handle high viscosity oils very effectively. The bag does not permanently

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1 retain a high level of useable oil within the bag when the bag is replaced. It also
reduces costs of disposal of the used extractor because the bag contains less oil after
draining; used oil is classified as a hazardous material which requires specialized and
costly handling. Smaller extractors containing less retained oil need to be disposed of
5 less frequently. Further, the present extractor, when used substantially to its sorption
capacity, includes very little void space and so need not be shredded, as is required for
pleated filters for efficient disposal.

When used with oils with and without oil dispersing additives within the oil,
10 it has been found, using established ASTM testing procedures, that an extractor
according to the present invention produce substantially lower residual water levels in
lubricating oils than do previously known extraction devices. In tests using gear oil
containing no water dispersal agent, an extractor according to the present invention
extracted 1600 ml. (added to the oil periodically in 200 ml. increments) of water out
15 of the oil and never went above 0.02% residual water with a flow rate of 1 gallon per
minute. Furthermore, when tested with a sophisticated, high viscosity aircraft engine
oil containing substantial levels of water dispersant additive, the extractor extracted
1200 ml of water (added to the oil in the same manner) and never went above 1%
20 residual water with a flow rate of 1 gallon per minute; in that instance, the usual
residual water level was .5% or lower.

The present extractor can be used on a large variety of lubricating oils. The
present extractor operates on a higher viscosity oil than the prior art fiberglass laminate
filter in which performance drops off as oil viscosity increases. For example, it has
25 been found that the present extractor, unlike the prior art filters, can operate effectively
on an oil with a kinematic viscosity greater than 350 Saybolt Seconds Universal.

The features and benefits reviewed above are provided in a low-cost extractor
element which readily retrofits into existing canister assemblies commonly used in oil
recirculating systems.

30 As noted above, the presently preferred sorption medium useful in the practice
of the invention is Hoechst/Celanese polymer IM-1000 as converted into a tissue-faced
laminated sheet material, product 9503, by Gelok International Corp. Polymer
IM-1000 is a sodium polyacrylate polymer. A potassium polyacrylate polymer
35 obtained from the same source has been found to be useful to extract water from oil,
but not as effectively as the sodium salt of acrylic acid. Such polymers are referred
to broadly as cornstarch grafted polyacrylates. To the extent that salts of acrylic acid,

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1 salts of other organic acids, and other substances are useful to extract one liquid from
another, such organic acid salts and other substances can be used in extraction elements
according to this invention to extract a variety of liquids from dispersion or suspension
in other liquids.

5 The described embodiment of the invention is only preferred and illustrative
of the inventive concept; the scope of the invention is not to be restricted to such an
embodiment. Other arrangements may be devised by one skilled in the art without
departing from the scope of the invention.

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WHAT IS CLAIMED IS:

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1. A water extraction element comprising:
a bag having a closed bottom and an open top;
a bag support proximate the top of the bag; and
at least one layer of water-sorbing material essentially fully covering
an inner surface of the bag, at least a portion of the water-sorbing material being
present in the bag in filaments which depend from adjacent the bag support into the
bag.

2. The apparatus of claim 1 in which the bag comprises a felt material
folded and stitched into a bag-shape.

3. The apparatus of claim 2 in which at least one continuous layer of
water-sorbing material lines an interior surface of the felt.

4. The apparatus of claim 1 in which the filaments of water-sorbing
material are longer from their upper ends to their opposite ends than the length of the
bag from the location of the filament upper ends to the bottom of the bag.

5. The apparatus of claim 1 in which the filaments of water-sorbing
material are defined by a folded sheet of water-sorbing material having slits between
end margins of the sheet.

6. The apparatus of claim 5 in which a plurality of slit and folded sheets
of water-sorbing material are arranged in staggered layers within the bag.

7. The apparatus of claim 1 in which the bag support comprises a wire
ring.

8. The apparatus of claim 1 in which at least one layer of water-sorbing
material includes a superabsorbing polymer.

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1 9. The apparatus of claim 8 wherein the polymer comprises a polyacrylate.

5 10. The apparatus of claim 9 wherein the polymer comprises a sodium polyacrylate polymer.

10 11. The apparatus of claim 8 in which the polymer is granular and forms an inner layer of a laminate which includes tissue sheets on opposite sides of that inner layer.

15 12. A method for extracting water from oil comprising the steps of:
 flowing wet oil having a dispersed water component into a porous container;
 providing a water-from-oil sorber within the container in a form in which the
 sorber is carried in a slit sheet-like medium formed into a plurality of finger-like
 elements which allow the sorber to expand substantially inwardly of the container
 toward the direction of oil flow; and

20 flowing dry oil having a smaller water component relative to the wet oil out of the container.

25 13. The method of claim 12 in which the step of providing a water-from-oil sorber comprises providing a bag-type water-sorbing element in which the plurality of finger-like elements is contained within a bag comprised of a sheet of felt and at least one sheet of unslit sorber material.

30 14. A device for extracting water from dispersion in a non-aqueous liquid comprising:

 a porous bag having a closed bottom, an open top with which is associated means for supporting the bag, and

35 at least one layer of water-sorbing material essentially fully covering the inner surface of the bag, at least a portion of that material being present in the bag as discrete bodies of the material which are free to move toward the interior of the bag in response to enlargement of the bodies due to sorbtion of water by the bodies.

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1 15. A method of fabricating a device for extracting from a first liquid a second liquid dispersed in the first liquid, comprising the steps of:

 providing at least one sheet of sorbtion material which includes a substance having the ability to extract the second liquid from dispersion in the first liquid;

5 forming the sheet of sorbtion material to define a plurality of strips of the material which extend integrally from at least one of two opposite end margins of the sheet;

 providing a supporting bag having an open end and a closed end formed of a material which is porous to the first liquid;

10 inserting the formed sheet of sorbtion material into the bag so that the strips extend into the bag around the interior thereof from adjacent the open end of the bag, and

 affixing at least the one end margins of the formed sheet to the bag adjacent the open end of the bag.

15 16. The method of claim 15 in which the steps of providing a supporting bag includes providing in the bag a lining comprised of at least one substantially continuous layer of said sorbtion material.

20 17. The method of claim 15 in which the forming step comprises forming the strips along a central portion of the sheet between but not through the opposite end margins of the sheet, and including the further step of folding the sheet so that the end margins thereof are substantially registered, which further step is performed before performance of the inserting step.

25 18. The method of claim 17 including forming by a slitting process a plurality of sheets of sorbtion material according to the forming step described in claim 17, performing the folding step upon each formed sheet, and including the still further step of arranging the folded sheets in the bag in an overlying relation in which the end margins of the several sheets are substantially registered and in which adjacent folded sheets are offset along the margins of each sheet adjacent thereto so that the strips in each sheet cover the slits in each adjacent sheet.

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1 19. The method of claim 18 including performing the arranging step before
insertion of any sheet into the bag.

5 20. The method of claim 15 wherein the strips are defined to have effective
lengths greater than the length of the bag from its open end to its closed end.

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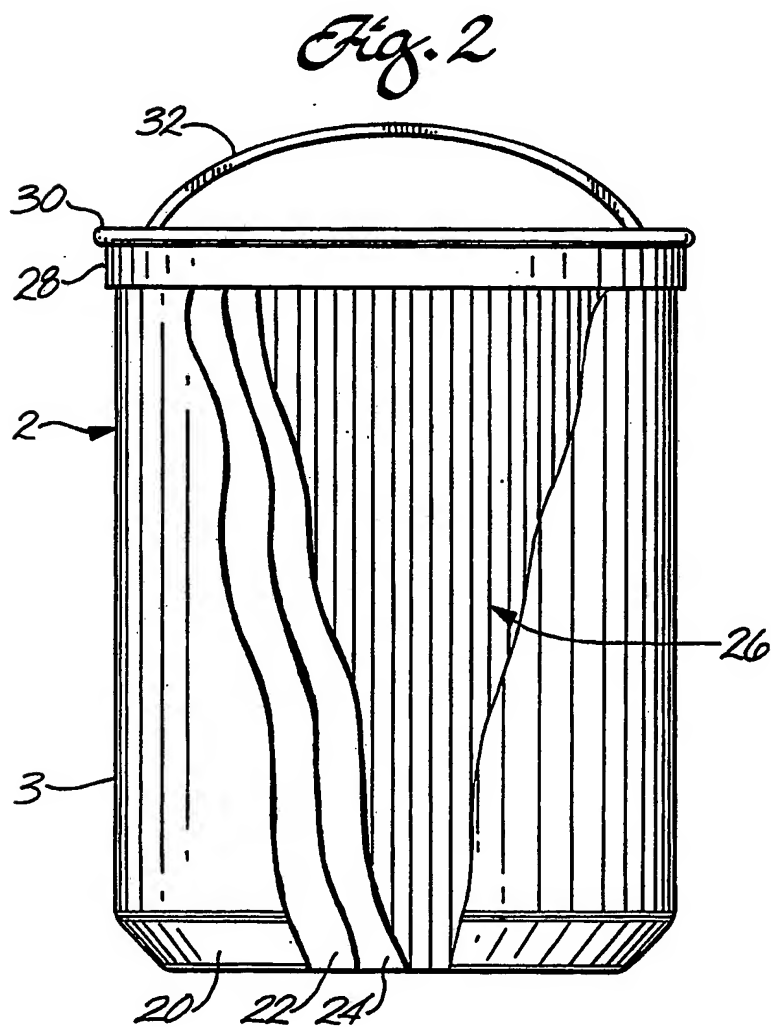
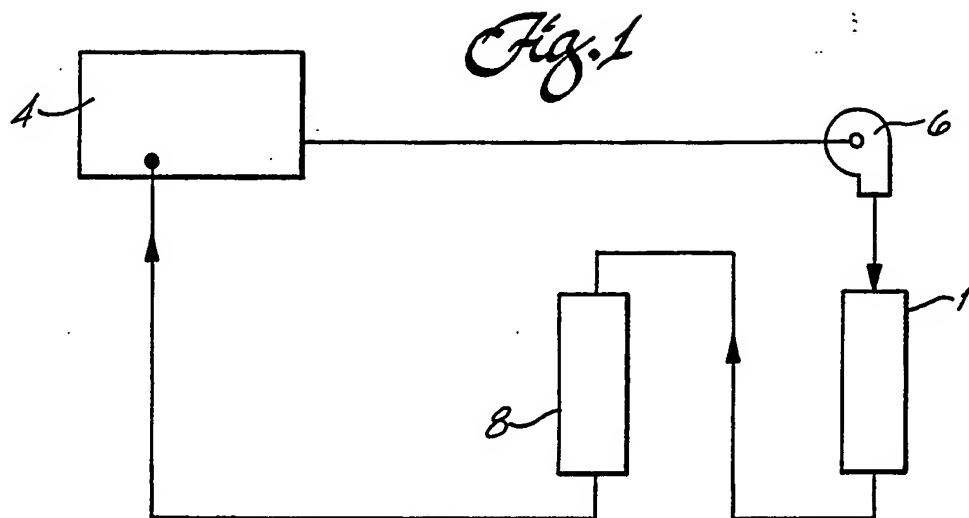
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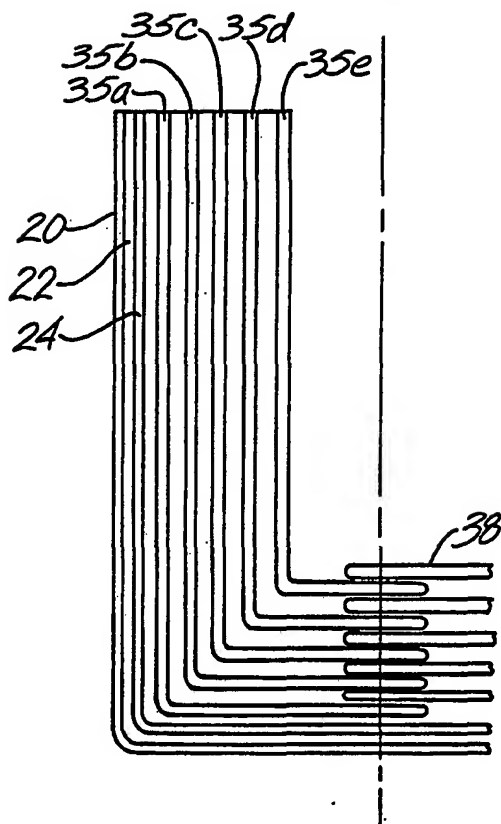


Fig. 4

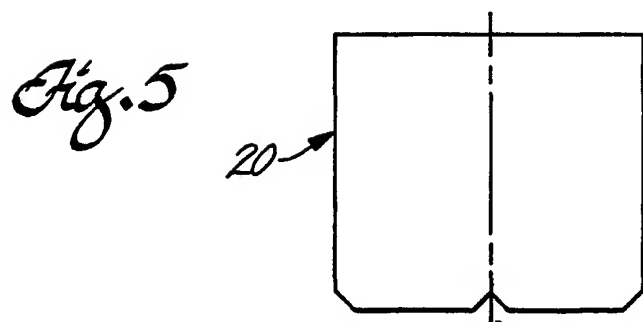


Fig. 6

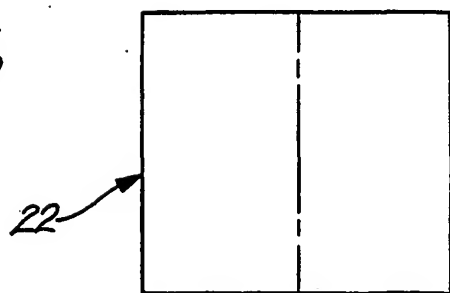


Fig. 7

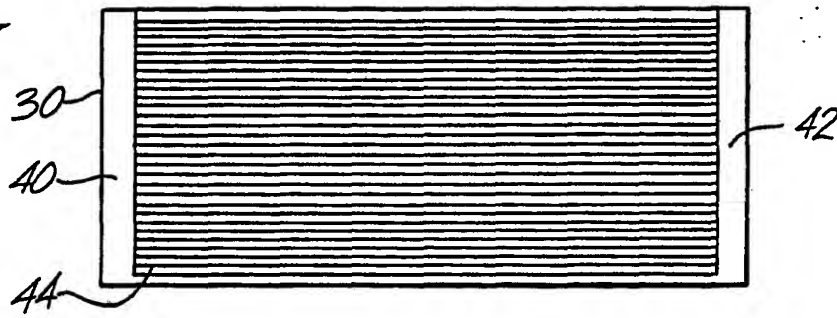


Fig. 8

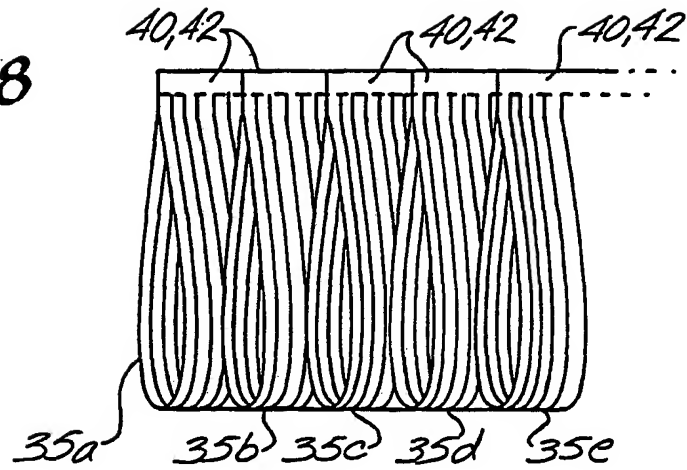


Fig. 9

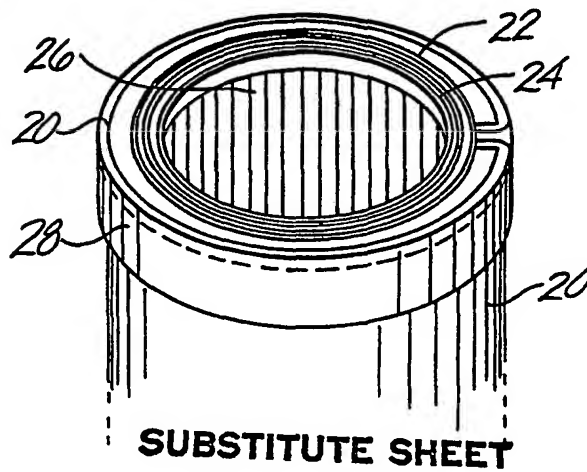
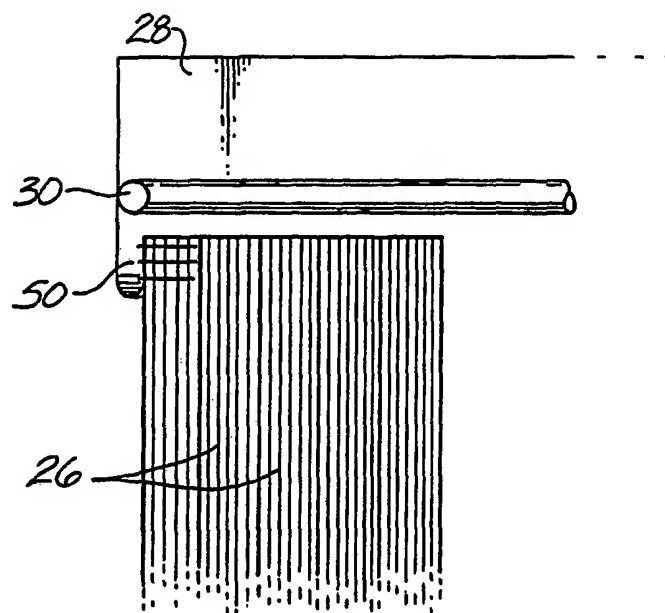
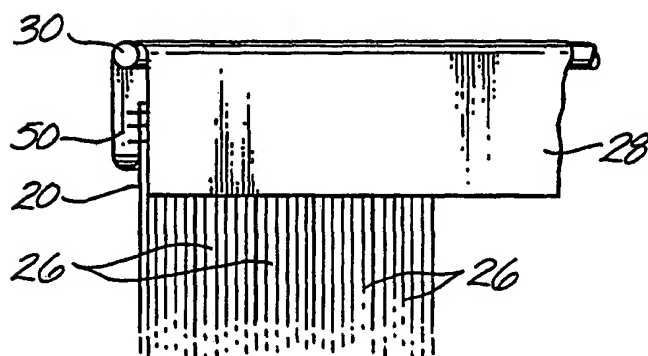


Fig. 10*Fig. 11***SUBSTITUTE SHEET**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/03428**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B01D 29/11

US CL :210/484, 495, 689; 264/146

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/497.01, 502.1; 264/160

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,747,960 (FREEMAN ET AL) 31 May 1988, see entire document.	1-14
A	US, A, 4,758,350 (PITTS ET AL) 19 July 1988, see entire document.	1-14
Y	US, A, 4,787,949 (COLE ET AL), see entire document.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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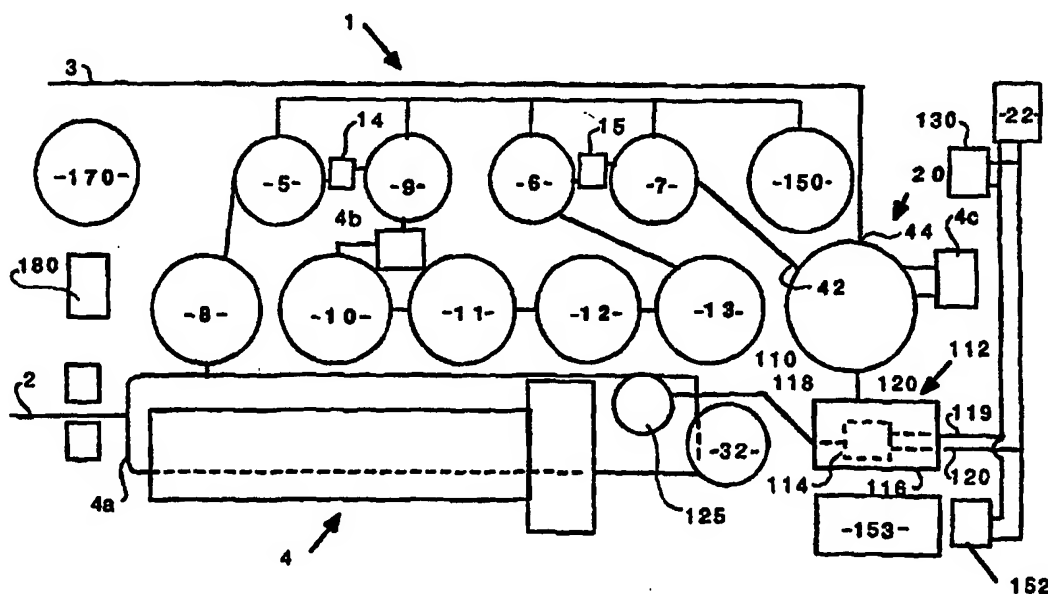
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<p>(21) International Application Number: PCT/NZ95/00006</p> <p>(22) International Filing Date: 20 January 1995 (20.01.95)</p> <p>(30) Priority Data: 248244 23 January 1994 (23.01.94) NZ</p> <p>(71)(72) Applicant and Inventor: GILBERT, Ronald, James [NZ/NZ]; 32 Amante Crescent, Mairangi Bay, Auckland 1310 (NZ).</p> <p>(74) Agents: WELLS, Ceri, P., K. et al.; 29 Clarence Street, P.O. Box 759, Hamilton 2001 (NZ).</p>	<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

(54) Title: **LIQUID TREATMENT APPARATUS**

(57) Abstract

A process and apparatus for treating contaminated liquids for reuse incorporating filtering and degasifying. The process enables the decontamination and degasifying to be carried out away from or at the site of the contaminated liquid and includes means by which filtering materials can be automatically replaced.

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Liquid Treatment Apparatus

TECHNICAL FIELD

This invention relates to a liquid treatment apparatus and methods of treating liquids using such an apparatus. For convenience only, the present invention will be described with reference to liquid treatment apparatus and methods for the treatment of liquids such as transformer oils for which the invention may be particularly applicable. However, it is to be understood that it is not to be limited as such. Moreover, because the invention may have other applications it is to be understood that the prior art and possible embodiments of the invention as discussed below are given by way of example only.

BACKGROUND ART

Conventional apparatus and methods for the treatment of transformer oils which have become contaminated with contaminants such as water, acidic compounds, other products of oxidation and colloidal contaminants generally involve heating and filtering the oil, treatment with an adsorbent such as Fuller's earth to adsorb contaminants from the oil, and subsequently degasifying the oil. Additional processes such as passing the liquid through a coalescer to coalesce water in the liquid and hence separate it out, and/or centrifuging the liquid to remove free water may also be incorporated into the operation.

Heating is generally carried out by electrical heating with an element immersed in the oil. However, due to the relatively high temperature of the element required to obtain adequate heat transfer to the oil, overheating of the oil can occur at the surface of the element with the

formation of additional impurities.

Centrifuging to remove the water can have adverse effects on the liquid due to the centrifugal loadings and shear stresses to which the liquid is subjected which can affect the chemical chains of molecules and alter the
5 liquid properties.

Furthermore, with conventional apparatus and methods, the adsorbent which is contained in an adsorbent container has a limited life and must be periodically replaced. However, due to the tendency for conventional adsorbents such as Fuller's earth to coalesce together in the container,
10 replacement of the spent adsorbent generally requires manual removal. Hence full automation of the liquid treatment method and apparatus is not possible, and labour and operating costs can be high. Moreover, the adsorbent replacement generally results in loss of any liquid remaining in the adsorbent.

15 Conventional methods of degasifying the oil subsequent to filtering and adsorption treatment generally involve holding the oil in a container as a single body of liquid and subjecting this to a vacuum so that contaminants boil off and come out of solution. Since it takes time for complete degasification by this method, the oil is generally recirculated
20 through the system several times until the required degree of purity is obtained. This requirement for recirculation involves additional time and hence adds to the costs and inconvenience of treating the oil.

The above disadvantages of the conventional methods and apparatus for the treatment of oils thus result in a relatively expensive operation which
25 cannot be easily automated.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example
5 only.

DISCLOSURE OF THE INVENTION

According to the present invention there is provided a process for treating contaminated liquids, said process comprising the steps of;

- 10 (a) passing said contaminated liquid through a filter to remove particles from said liquid,
- (b) heating the filtered liquid in a heater;
- (c) passing said heated liquid through an adsorber containing a granular adsorbent capable of removing contaminants from said liquid; and
- 15 (d) degasifying the liquid.

The process may include the steps of;

- (a) isolating a container containing granular material from an inlet and outlet,
- 20 (b) applying a pressure differential across granular material contained in said container,
- (c) allowing liquid contained in said container to flow out of said container through a liquid outlet as a result of said pressure differential, while preventing granular material in said container from flowing out of said container,
- 25 (d) closing off said liquid outlet ,

- (e) discharging said granular material from said container by opening a granular material discharge outlet to allow granular material contained therein to flow out of said container under a pressure differential,
 - 5 (f) closing said granular material outlet and reducing the pressure in said container, and
 - (g) opening a granular material inlet to said container to allow a predetermined amount of granular material to flow into said container.
- 10 The process may further include said step of applying a pressure differential across said granular material involves pressurising an inlet to said container and connecting said liquid outlet from said container to a collection chamber (buffer collection tank), and the step of discharging granular material from said container involves allowing a pressure
- 15 inside said container to increase to a predetermined pressure above atmospheric pressure, and then opening said discharge outlet to discharge granular material under the resultant pressure differential into a container at atmospheric pressure, and recycling liquid collected in said collection chamber back into said liquid treatment apparatus.
- 20 The process may include degasifying comprises the steps of;
- (a) heating a liquid to be treated to a predetermined temperature, and then passing said liquid into a container maintained at a reduced pressure,
 - (b) causing said liquid to flow over a surface or surfaces inside said
- 25 container as a thin film, so that liquid contaminants contained in said liquid evaporate from said liquid, and gaseous contaminants dissolved in said liquid come out of solution and separate from said

liquid, and until a predetermined purity of liquid is obtained, and
(c) pumping said purified liquid from said container.

According to a further aspect of the present invention there is provided a liquid treatment apparatus for removal of contaminants from a liquid,
5 said apparatus comprising:-

- inlet means for inputting a liquid to be treated by said apparatus into said apparatus,
outlet means for discharging said liquid from said apparatus after treatment by said apparatus,
10 heating means for heating said liquid,
filter means for filtering contaminants from said liquid,
adsorption means for adsorbing contaminants from said liquid,
evaporator/degasifier means for evaporating and separating out liquid and gaseous contaminants contained in said liquid,
15 pumping means for pumping said liquid from said inlet means through said filter means, adsorption means, heating means, and evaporator/degasifier means to said outlet means, and
control means for controlling the operation of various components of the apparatus to enable semi automatic or fully automatic operation.
- 20 The apparatus may further comprise coalescer means for coalescing liquid impurities in said liquid for subsequent removal from said liquid.

The apparatus may further comprise material handling means for facilitating replacement of adsorbent/filter material in said filter means and said adsorber means.

Said heating means may comprise a heat source for heating a primary heating fluid, and a heat exchanger for exchanging heat from said primary fluid to said liquid being treated.

The evaporator/degasifier means may comprise;

- 5 a vacuum chamber having an inlet and an outlet,
means for producing a vacuum in said vacuum chamber, and
means for producing a thin film flow of said liquid inside said vacuum chamber.

- The heating means for the liquid treatment apparatus according to the
10 present invention may comprise an oil burner type heater for heating a primary heating medium, and one or more heat exchangers for transferring heat from the primary medium to the liquid being treated. With such an arrangement the temperature of the secondary heat transfer surfaces may be easily controlled to ensure it does not exceed an
15 amount which would be detrimental to the liquid being treated. For example with the treatment of transformer oils this temperature would be kept below 60°C.

- Heat exchangers may be provided at different stages of the treatment process to obtain optimum temperature conditions. For example, a first
20 higher temperature heat exchanger may be provided for heating liquid in the evaporator/degasifier, a second medium temperature heat exchanger may be provided for heating liquid at the inlet, and a third lower temperature heat exchanger may be provided intermediate in the process to maintain a suitable temperature of the liquid.

The filter/adsorber means may comprise a container filled with a granular adsorber/filter material, the container having a liquid inlet and outlet, and a granular material inlet and outlet. The liquid outlet may have a screen for containing granular material in the container while
5 allowing liquid to pass from the container to the liquid outlet. A suitable material for the adsorber/filter may be a granular material such as Attapulgate™ mined by Malina Holdings in Australia. This material has been found to maintain its granular characteristics even when spent as an adsorbent, and so can be easily flushed from the container, thus
10 making it suitable for an automated material handling system.

In addition, standard types of commercial filters may be used for filtering contaminants from the liquid. For example a proprietary type of industrial filter such as a Zeta Plus® filter having a filter media with a high contaminant holding capacity may be suitable. Several such filters
15 may be used arranged in series with provision for isolation of any one filter to enable the filter element to be changed when required. A filter condition indicator may be incorporated into a control system of the apparatus to indicate when the element requires changing.

With the evaporator/degasifier according to the present invention, the
20 vacuum producing means may comprise a pump such as a lobe type or star type hydraulic pump. This may be housed inside a sealed container with an outlet from the container connected to an outlet from the pump, and an inlet to the container connected to the vacuum chamber of the evaporator/degasifier. Housing the pump inside the sealed container
25 helps to overcome problems with vacuum sealing. Hydraulic lines for powering the pump may be passed through sealed openings in the wall of the container. With such an arrangement a vacuum of at least 5 Torrs

may be applied to the vacuum chamber of the evaporator/degasifier.

The means for thin film flow production in the evaporator/degasifier may comprise a plurality of elongate tubes arranged in vertical orientation adjacent to each other, the tubes being supported at an upper end thereof
5 by a baffle plate which is fixedly attached to the vacuum chamber and which seals a passage between the tubes so that liquid can only flow though the tubes in a downward direction. An additional baffle plate may also be provided at the lower end of the tubes so as to seal the outer surface of the tubes. A heating liquid may then be circulated around the
10 tubes to heat or maintain the temperature of the liquid as it flows down the tubes. Preferably the tube diameter and length dimensions would be chosen to provide a thin film of a suitable surface area and thickness to enable impurities to be removed under the vacuum while the liquid flowed through the evaporator/degasifier. Having a flow length (tube
15 length) of 1200 mm under a vacuum of 9.5 Torr with a liquid temperature of approximately 55°C may be sufficient to reduce the residual gas/liquid impurities in the liquid to a sufficient amount, so that the liquid treatment apparatus can treat the liquid in a single pass.

Preferably the openings to the vertically orientated tubes are disposed
20 above the surface of the baffle plate.

The coalescer may comprise a standard coalescer for removal of liquids from a liquid.

The material handling means may comprise;

(a) a pressurisation system for applying a pressure across the
25 adsorber/filter container between the inlet and outlet,

- (b) evacuation means such as a vacuum fan for reducing a pressure inside the container,
- (c) a first valve for selectively opening/closing the container liquid inlet to a liquid supply,
- 5 (d) a second valve for selectively opening/closing the container granular material inlet to a granular material supply,
- (e) a third valve for selectively opening/closing a container pressurisation inlet to the pressurisation system,
- (f) a fourth valve for selectively opening/closing a container evacuation
10 inlet to the evacuation means,
- (g) a fifth valve for selectively opening/closing the container liquid outlet to a liquid outlet,
- (h) a sixth valve for selectively opening/closing the container liquid outlet to a liquid buffer container,
- 15 (i) a seventh valve for selectively opening/closing the container granular material outlet to a spent material dump container, and
- (j) a control system for controlling an opening/closing sequence of the valves such that liquid contained in the granular material is first forced out of the container under pressure from the pressurisation
20 means into the liquid buffer container, granular material is then forced out of the container into the spent material dump container, and then granular material is drawn into the container from a granular material supply via the granular material inlet.

The material handling means may also incorporate valving and controls to facilitate the replacement of filter or coalescer elements. Such equipment may involve valving to isolate the container having the element to be changed, and piping to drain off a predetermined amount of
5 liquid from the container into the above-mentioned liquid buffer container to allow space for a new dry filter or coalescer element to be inserted without spilling. With both the filter/adsorbent change and the filter/coalescer change, liquid contained in the buffer container may be recycled back into the system for treatment thereby avoiding waste, and
10 enabling continuous operation of the apparatus.

The pressurisation system for the material handling means may comprise one or more compressors which may be electrically or hydraulically driven, arranged to apply a positive pressure to the inlet of the adsorber/filter container. A negative pressure may be produced on
15 the outlet of the container by drawing a vacuum on the liquid buffer container. With this arrangement the pressure inside the filter/adsorber container may be kept to a minimum thereby enabling simpler design and manufacture.

The evacuation system for the material handling means may comprise a
20 suction fan drawing from the adsorber/filter container and discharging into a dust collector. The granular material inlet to the container may be arranged so that a cyclone type flow pattern is produced, with the granular material dropping down into the container and the air being drawn out from a central outlet in the top of the container.

The granular material supply for the materials handling means may include a storage hopper for storing a predetermined amount of granular material ready for charging into an adsorber/filter container. This hopper may be maintained in a full condition by a separate valving
5 means which opens the hopper to the evacuation means whereby a vacuum is produced in the hopper to enable granular material to be drawn into the hopper through an inlet pipe from a granular material supply tank.

The liquid buffer container for the material handling means may be a
10 cylindrical container of sufficient capacity to hold at least the amount of liquid discharged from a filter/adsorber during adsorbent replacement, and preferably also the amount of liquid discharged at the time of a filter/coalescer change. The buffer container may be provided with a control system and valving to enable the liquid inside to be recycled back
15 into the liquid treatment apparatus.

The valves in the materials handling means may preferably be two way or three way valves so that closing of one valve automatically opens another valve. The sixth valve (dump valve) for dumping the spent material may preferably be a large bore ball valve. The screen for
20 retaining the granular material at the bottom of the container may comprise a cylindrical screen arranged coaxial with an axis of the bore of the dump valve, and sealed at its upper and lower peripheral edges so as to prevent granular material from passing the screen to a liquid outlet.

The pumping means for the liquid treatment apparatus may comprise conventional liquid pumps. These may be electrically or hydraulically operated. Having hydraulically operated pumps may be preferable in that a single hydraulic pressure supply powered by the engine of a vehicle on which the apparatus is mounted may be used to provide power for the pumps, blowers/fans and other equipment.

The control means for the liquid treatment apparatus may comprise a programmable logic controller whereby the condition of the various components such as filters, adsorbers, the evaporator/degasifier, the heater, may be monitored and the various, valves, pumps, compressors, blowers, fans etc. may be operated to maintain the desired operating conditions, and to control replenishment of the granular adsorber material. The apparatus may thus be programmed to operated semi automatically or automatically depending on requirements.

15 BRIEF DESCRIPTION OF THE DRAWINGS

Further aspects of the present invention will become apparent from the ensuing description which is given by way of example only and with reference to the accompanying drawings in which:

Figure 1: is a schematic plan view of a liquid treatment apparatus according to an embodiment of the present invention;

Figure 2: is a schematic view from a right side of the liquid treatment apparatus of FIG. 1 showing details of a heating system and an arrangement of filter/adsorber towers and an evaporator degasifier;

- Figure 3: is a schematic view from the right side of the liquid treatment apparatus of FIG. 1 showing an arrangement of granular material inlet and outlet valves for the filter/adsorber towers;
- 5 Figure 4: is a schematic sectional view of a lower part of a filter/adsorber tower showing an arrangement of a screen element and a rotary discharge valve;
- Figure 5: is a schematic view from a left side of the liquid treatment apparatus of FIG. 1 showing an arrangement valves for the
10 filters and coalescer;
- Figure 6: is a schematic view from a left side of the liquid treatment apparatus of FIG. 1 showing an arrangement of pressurisation valves for the filter/adsorber towers;
- Figure 7: is a schematic sectional view of a filter/adsorber tower
15 showing an arrangement valves;
- Figure 8: is a cross-sectional view of aspects of the filter/absorber tower of Figure 7, and

Figure 8A: is an enlarged view of the encircled portion of Figure 8.

BEST MODE FOR CARRYING OUT THE INVENTION

- 20 In Figure 1, there is shown a schematic plan view of a liquid treatment apparatus according to an embodiment of the present invention generally indicate by arrow 1. The apparatus 1 which is mounted on a truck or trailer (not shown in the figures) comprises an inlet 2 for inputting liquid to be treated by the apparatus 1 into the apparatus 1, an outlet 3 for

discharging the liquid from the apparatus 1 after treatment by the apparatus 1, a heater generally indicated by arrow 4 for heating the liquid by means of heat exchangers 4a, 4b and 4c, element type filters 5, 6 and 7 and granular material filter 8 for filtering contaminants from the liquid, a coalescer 9 for coalescing liquid impurities in the liquid for subsequent removal from the liquid, adsorber towers 10, 11, 12 and 13 for adsorbing contaminants from the liquid, an evaporator/degasifier generally indicated by arrow 20 for evaporating and separating out liquid and gaseous contaminants contained in the liquid, a hydraulic power supply 22 (driven by the truck motor or an electric main drive) for providing hydraulic power for the apparatus, and hydraulically driven pumps 14, 15 etc. for pumping liquid from the inlet 2 through the medium temperature heat exchanger 4a, filters 8, and 5, coalescer 9, lower temperature heat exchanger 4b, adsorbers 10, 11, 12, 13, filters 6 and 7, and evaporator/degasifier 20 to the outlet 3.

The heater 4 as shown in more detail in FIG. 2 comprises a Thermix™ oil heating system 30 wherein a primary liquid is heated by an oil burner supplied with diesel fuel from a fuel tank 32, and passed to a heat exchanger 34 which has primary heating liquid pipe coils supported inside and which is filled with the liquid to be treated by way of an inlet 36 and 38. Additional primary heating coils are also connected to the lower temperature heat exchanger 4b and the higher temperature heat exchanger 4c. A control system is provided (not shown in the figures.) for controlling the output from the burner so as to maintain an outlet temperature from the heat exchanger of between 20°C to 75°C.

As shown more clearly in FIGS 2 and 3, the filter tower 8 and adsorber towers 10, 11, 12, 13 are in the form of upright cylindrical containers. These are filled with a predetermined amount of Attapulgate™ granular adsorbent material. Each of the towers is provided respectively with
5 liquid inlets 40, 42, 44, 46, 48 and outlets 50, 52, 54, 56, 58, and granular material inlets 60, 62, 64, 66, 68 and outlets 70, 72, 74, 76, 78.

As shown more clearly in FIG. 4 which gives details of the outlet region for filter tower 8 which is typical of the outlets for the adsorber towers 10, 11, 12, 13, the liquid outlet 50 has a cylindrical screen 80 for containing
10 granular material 82 in the tower 8 while allowing liquid to pass from the tower 8 to the liquid outlet 50. A dump valve 84 in the form of a large bore ball valve for dumping the spent granular material 82 is mounted beneath the screen 80 at the granular material outlet 70. The screen 80 is
15 arranged coaxial with an axis of the bore of the dump valve 84 and is sealed at its upper and lower peripheral edges 84, 86 so as to prevent granular material 82 from passing the screen 80 to the liquid outlet 50.

Commercial Zeta Plus® filters made by Process Filtration Products of the USA having a filter media with a high contaminant holding capacity are used for the element filters 5, 6, 7 shown in FIG. 5. Filters 5 and 6 are both
20 fitted with 5 to 10 micron mesh cartridges, filter 7 is fitted with a 5 to 7 micron cartridge, and the coalescer which operates at an approximate pressure differential of 15psi is fitted with a coalescer cartridge. As shown in FIG. 5, the filter 5, coalescer 9, and filters 6 and 7 are each provided with respective inlets 90, 92, 94, 96 and outlets 91, 93, 95, 97, with
25 filters 6 and 7 connected in series. Any one of the filters or coalescer may be isolated by means of isolation valves 100, 102, 104, 106 and 101, 103, 105, 107 provided on the respective inlets and outlets so that the filter element or

coalescer element can be changed when required without interrupting the operation of the apparatus. Outlets from the filters can be directed to the buffer collector tank 150 by means of the outlet isolation valves 101,103,105,107 so that the filter/coalescer case can be drained a certain amount to avoid overflow when a new element is fitted. Filter condition indicators (not shown in the figures.) are incorporated into a control system of the apparatus to indicate when the filter elements or coalescer element require changing.

The evaporator/degasifier 20 as shown in FIG.1 and in more detail in FIG. 5 comprises a vacuum chamber 110 having an inlet 42 and outlet 44, an evacuating device generally indicated by arrow 112 (FIG.1) for producing a vacuum of up to 10Torr in the vacuum chamber 110, and a bank of thin tubes generally indicated by arrow 114 . As shown in FIG. 1 the evacuating device 112 comprises a lobe type or star type hydraulic pump 114 housed inside a sealed container 116, with an outlet 118 from the container connected to an outlet from the pump 114 and an inlet 120 to the container connected to the vacuum chamber 110 of the evaporator/degasifier. The outlet 118 discharges into a second buffer tank 125 for subsequent return to the system. Hydraulic lines 119,120 for supplying power from the hydraulic pump 22 to power the pump 114 are passed through sealed openings in the wall of the sealed container 116.

The tubes 114 in the vacuum chamber 110 are arranged in vertical orientation adjacent to each other, and supported at upper and lower ends by baffle plates 130, 131 respectively which are fixedly attached to the vacuum chamber 110 and which seals a passage between the tubes 114 so that liquid can only flow through the tubes 114 in a downward direction. Heating liquid surrounding the tubes 114 is heated by the higher

temperature heat exchanger 4c. In the present embodiment 152 tubes made from 20mm inside diameter stainless steel 1200 mm long are provided inside the chamber 100, so that with a flow rate of 30 litres per minute a film thickness of approximately 5-15 microns is obtained, and
5 under a vacuum of 9 - 10 Torr and a temperature of 50°C the residual gas/liquid impurities in the liquid can be reduced to a sufficient amount, so that the liquid treatment apparatus 1 can treat the liquid in a single pass.

The material handling system for replenishment of the adsorbent/filter
10 material contained in the filter tower 8 and adsorber towers 10, 11, 12, 13 comprises a pressurisation system having a hydraulically driven compressor 130 (FIG. 1) which can be selectively connected to the respective towers 8,10,11,12,13 by means of three way valves 140,142,144,146, 148 (FIG. 6). A negative pressure can be applied to the
15 respective towers 8,10,11,12,13 by connecting their respective liquid outlets 50,52,54,56,58 (FIG. 3) to a liquid buffer container 150 (FIG. 1) in which a negative pressure has been produced by the evacuating device 112. With this arrangement a differential pressure across the adsorbent/filter material of from 30psi to 2psi may be produced while maintaining the
20 pressure inside the tower below 30psi. Hence the tower is not required to conform to stringent pressure vessel design standards thereby reducing design and manufacturing costs.

A hydraulically driven induction fan 152 (FIG. 1) discharging into a dust collector 153, is connected by means of the three way valves
25 140,142,144,146,148 (FIG.6) to evacuation outlets 160,162,164,166,168 (FIG. 3) of the respective containers 8,10,11,12,13. This provides a low pressure to draw the granular filter/adsorber material into the tower via the

respective inlets 60,62,64,66,68 (FIG. 3) when the valve is turned to open the tower to the induction fan 152. The arrangement of the evacuation outlets of the towers is shown more clearly in FIG. 7 which shows an arrangement for tower 8 which is typical of the other towers 10,11,12,13.

5 In this arrangement, the granular material inlet 60 is provided on the side wall of the tower 8 while the evacuation outlet 160 is provided centrally in the top of the tower 8.

Granular material is selectively supplied to the respective tower 8,10,11,12,13 from a storage hopper 170 (FIG. 3) via a distributor valve 172.

10 The distributor valve 172 comprises a rotatable disk with internal passages arranged so as to align with respective outlets to the towers depending on a selected rotation of the disc. The storage hopper 170 is filled with sufficient material for replacement of one tower by connecting a central upper outlet to the induction fan 152 to thereby draw in

15 granular material from a supply tank which may be on a trailer towed behind the liquid treatment apparatus.

The before-mentioned liquid buffer container 150 of the present embodiment has a capacity to hold the total volume of liquid drained from one tower as well as the total volume of liquid from one of the filters or the

20 coalescer. Hence spillage which can occur when replacing a filter/coalescer element can be avoided by first lowering the level in the filter/coalescer casing. Additional provision is also provided for spillage in the form of a sump tank 175 (FIG. 2) which collects any spillage or leakage and recycles this back into the apparatus 1. Both the dump

25 container 150 and the sump tank 175 are provided with level sensors and valving so that when a predetermined level is reached the liquid is pumped back into the apparatus 1.

Operation of the various components of the apparatus such as valves, motors, pumps and compressors is controlled by a Programmable Logic Controller 180 mounted at the rear of the apparatus 1.

With respect to Figures 8 and 8a of the drawings provides means for
5 producing a thin film flow by providing a liquid flow path provided by the vertically orientated tubes 114 supported by baffle plates 130,131. As indicated in the Figures the openings to the vertically orientated tubes are disposed above the baffle 130 so that a thin film of liquid is drawn from the surface of the baffle plate, initially upwards and then over the top surface
10 of each tube in the manner indicated by Figure 8a. The extent to which each tube end extends above the surface of the baffle plate may be varied by design to suit different liquids but the arrangement has been found to provide an excellent even liquid film flow.

A description of an operation of the apparatus 1 of the present invention
15 for treating transformer oil will now be given with reference to the drawings.

The apparatus 1 which has been previously charged with transformer oil is first driven to a transformer installation requiring treatment of its insulation oil. The inlet 2 to the apparatus 1 is connected to the oil outlet
20 on the transformer casing and the outlet 3 from the apparatus 1 connected to the oil inlet on the transformer. The apparatus is then switched and the oil temperature in the primary heating coil of the heat exchanger brought up to a temperature of approximately 55°C. The circulating pump 14 is then switched on so as to circulate oil from the
25 transformer outlet, through the apparatus 1 and back to the transformer inlet. In this operation, the oil passes through the medium temperature heat exchanger 4a to warm the oil, the granular material filter tower 8 to

remove any larger particles and colloidal contaminants from the oil, the element filter 5 to remove smaller particles, the coalescer 9 to remove the majority of water, and then to the heat exchanger 4b where it is reheated to approximately 40°C. The oil then passes through adsorber towers
5 10,11,12,13 to further remove contaminants such as water, acidic compounds, and other products of oxidation. The oil then passes into the element filters 6 and 7 to remove very fine particles which may have been picked up in the adsorber towers.

Subsequently the oil flows through a pressure reduction valve into the top
10 of the evaporator/degasifier 20 where it is allowed to flow downwards as a thin film on the tubes 114 of the evaporator/degasifier 20 while being subjected to a vacuum of approximately 10Torr produced by the vacuum device 112. Remaining liquid and gases contained in the oil are evaporated off and removed from the oil so that a required degree of purity
15 is achieved. The oil is then pumped back to the inlet to the transformer completing the operation. Since the apparatus is able to achieve a satisfactory purification of the oil in one pass, the oil treatment operation is completed once the whole contents of the transformer have been circulated through the apparatus 1.

20 Replenishment of the adsorbent contained in the adsorbent towers 8, 10,11,12, and 13 will now be described. Adsorbent replenishment is called for after a predetermined period of operation determined by a timer in the programmable logic control unit 180.

At first a sufficient amount of clean adsorbent is loaded into the holding
25 hopper 170 using the induction fan 152 to reduce the pressure in the hopper 170 so that adsorbent may be drawn into the hopper through the inlet pip from a supply tank carried on a trailer behind the truck. The

filter/adsorber tower requiring replenishment is then isolated from the system by closing off the liquid inlet. The following description will be given in relation to filter/adsorber tower 8 as representative of the other towers 10,11,12,13. The liquid inlet valve 40 is thus closed off to isolate the tower 8 from the system. The liquid outlet 50 is then switched to bypass the system and open the outlet to the buffer container 150. The pressurisation valve 140 is then opened to allow the container to be pressurised to a pressure of 30psi thereby driving oil from the tower out via the bottom bypass valve to the buffer container 150. The outlet 50 isolation valve is then closed to allow the pressure in the tower to build up to 30psi. The bottom dump valve 84 then opens to allow the granular material contained on the tower to be ejected into an open container positioned close by. The pressurisation valve 140 is then closed and the bottom dump valve 84 closed. The top evacuation outlet 160 and granular material inlet 60 valves are then opened, and a blower which applies a pressure to the hopper 170 and the induction fan 152 are turned on to cause the adsorbent to be drawn from the hopper 170 into the tower. Once the tower has been filled with the charge from the hopper 170, the top evacuation outlet 160 valve and granular material 60 inlet valves close. A pump back valve then opens and a pump back pump is switched on for approximately 3 minutes to pump oil from the dump container 150 back into the tower. The pump back pump is then switched off and the inlet and outlet isolation valves opened so that the tower is connected back into the system.

25 In the above disclosure and description the material handling means and evaporator/degasifier means are incorporated into a liquid treatment apparatus. However the material handling means and evaporator/degasifier means of the present invention are not limited to

this application and may be used independently or respectively in other apparatus where granular material contained in containers is to be replenished, or where liquid containing liquid and gaseous impurities is to be purified.

- 5 For example the apparatus and methods may be applicable to the treatment of fuels such as jet fuel which require a high degree of purity especially from moisture which is susceptible to freezing at low operating temperatures.

I believe the advantages of my invention to be as follows, however it
10 should be appreciated that all such advantages may not be realised on all embodiments of the invention, and the following list is therefore given by way of example only as being indicative of potential advantages of the present invention. Furthermore, it is not intended that the advantages of the present invention be restricted to those of the list which follows.

- 15 1. The apparatus enables a fully automatic liquid treatment operation to be carried out.
2. The apparatus is self contained and portable and can be easily moved between treatment sites.
3. The use of a low cost granular material as a filter as well as an
20 adsorber helps reduce the filter load on more expensive element type filters.
4. The evaporator/degasifier enables single pass purification of the liquid thereby reducing operating costs and time.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

THE CLAIMS DEFINING THE INVENTION ARE:

1. A process for treating contaminated liquids, said process comprising the steps of;
 - (a) passing said contaminated liquid through a filter to remove particles from said liquid,
 - (b) heating the filtered liquid in a heater;
 - (c) passing said heated liquid through an adsorber containing a granular adsorbent capable of removing contaminants from said liquid; and
 - (d) degasifying the liquid.
2. The process of claim 1 including the steps of;
 - (a) isolating a container containing granular material from an inlet and outlet,
 - (b) applying a pressure differential across granular material contained in said container,
 - (c) allowing liquid contained in said container to flow out of said container through a liquid outlet as a result of said pressure differential, while preventing granular material in said container from flowing out of said container,
 - (d) closing off said liquid outlet ,
 - (e) discharging said granular material from said container by opening a granular material discharge outlet to allow granular material contained therein to flow out of said container under a pressure differential,
 - (f) closing said granular material outlet and reducing the pressure in said container, and

- (g) opening a granular material inlet to said container to allow a predetermined amount of granular material to flow into said container.
3. The process of claim 2, wherein said step of applying a pressure differential across said granular material involves pressurising an inlet to said container and connecting said liquid outlet from said container to a collection chamber (buffer collection tank), and the step of discharging granular material from said container involves allowing a pressure inside said container to increase to a predetermined pressure above atmospheric pressure, and then opening said discharge outlet to discharge granular material under the resultant pressure differential into a container at atmospheric pressure, and recycling liquid collected in said collection chamber back into said liquid treatment apparatus.
4. The process of any one of claims 1 to 3 wherein degasifying comprises the steps of;
- (a) heating a liquid to be treated to a predetermined temperature, and then passing said liquid into a container maintained at a reduced pressure,
 - (b) causing said liquid to flow over a surface or surfaces inside said container as a thin film, so that liquid contaminants contained in said liquid evaporate from said liquid, and gaseous contaminants dissolved in said liquid come out of solution and separate from said liquid, and until a predetermined purity of liquid is obtained, and
 - (c) pumping said purified liquid from said container.

5. A liquid treatment apparatus for removal of contaminants from a liquid, said apparatus comprising:-
inlet means for inputting a liquid to be treated by said apparatus into said apparatus,
outlet means for discharging said liquid from said apparatus after treatment by said apparatus,
heating means for heating said liquid,
filter means for filtering contaminants from said liquid,
adsorption means for adsorbing contaminants from said liquid,
evaporator/degasifier means for evaporating and separating out liquid and gaseous contaminants contained in said liquid,
pumping means for pumping said liquid from said inlet means through said filter means, adsorption means, heating means, and evaporator/degasifier means to said outlet means, and
control means for controlling the operation of various components of the apparatus to enable semi automatic or fully automatic operation.
6. A apparatus as claimed in claim 5, further comprising coalescer means for coalescing liquid impurities in said liquid for subsequent removal from said liquid.
7. Apparatus as claimed in claim 5 or claim 6, further comprising material handling means for facilitating replacement of adsorbent/filter material in said filter means and said adsorber means.

8. Apparatus as claimed in any one of claims 5 to 7 wherein said heating means comprises a heat source for heating a primary heating fluid, and a heat exchanger for exchanging heat from said primary fluid to said liquid being treated.
9. Apparatus as claimed in any one of claims 5 to 8 wherein said evaporator/degasifier means comprises;
a vacuum chamber having an inlet and an outlet,
means for producing a vacuum in said vacuum chamber, and
means for producing a thin film flow of said liquid inside said vacuum chamber.
10. Evaporator/degasifier means comprising a vacuum chamber having an inlet and an outlet, means for producing a vacuum in said vacuum chamber and means for producing a thin film flow of a liquid inside said vacuum chamber.
11. Evaporator/degasifier means as claimed in claim 10 wherein said means for producing a thin film flow incorporates a liquid flow path provided by vertically orientated tubes supported within said vacuum chamber by at least one baffle plate onto which the incoming liquid is introduced prior to passing through said tubes.
12. Evaporator/degasifier means as claimed in claim 11 wherein the surfaces of the vertically orientated tubes are heated.
13. Evaporator/degasifier means as claimed in claim 11 or claim 12 wherein openings to the vertically orientated tubes are disposed above the surface of the baffle plate.

14. A process substantially as herein described with reference to the accompanying drawings.
15. Apparatus substantially as herein described with reference to the accompanying drawings.

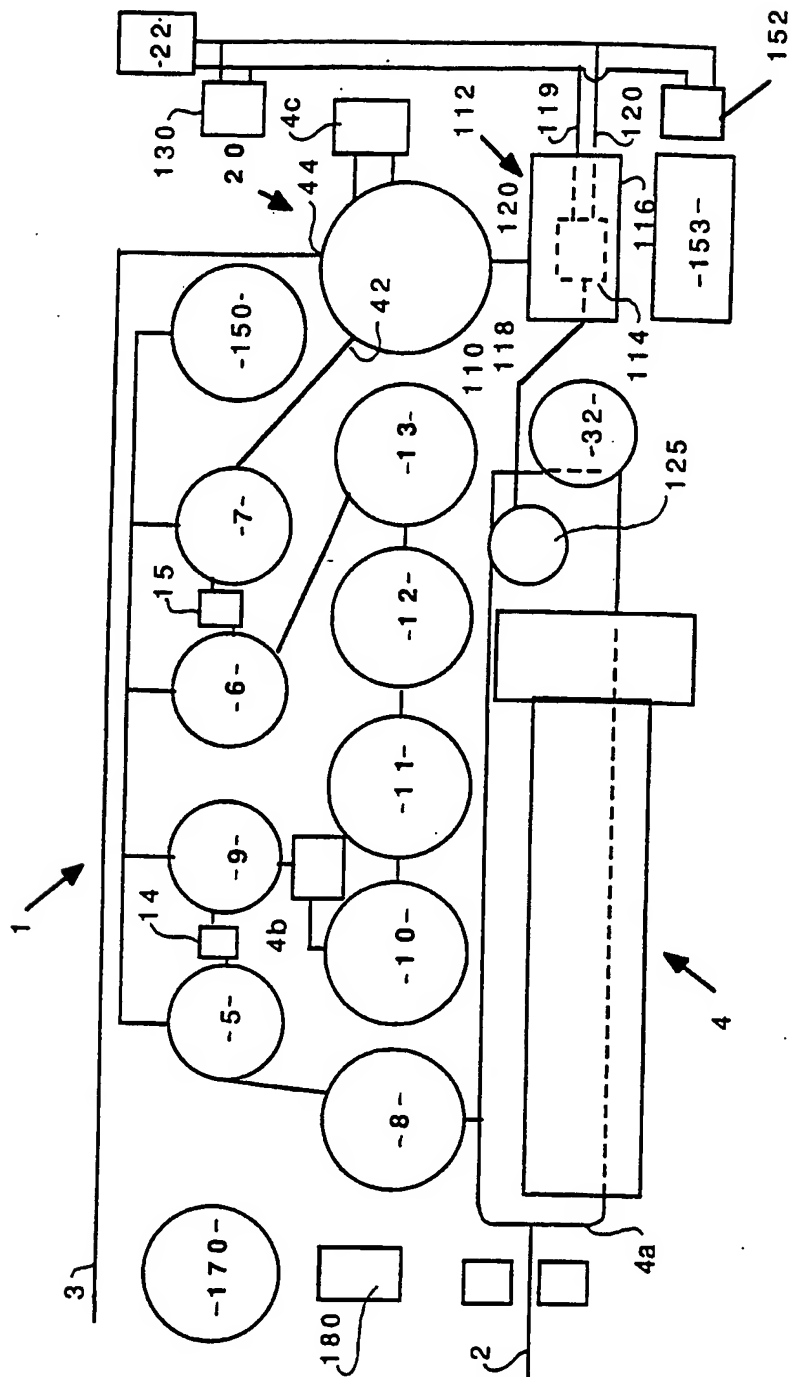


FIGURE 1

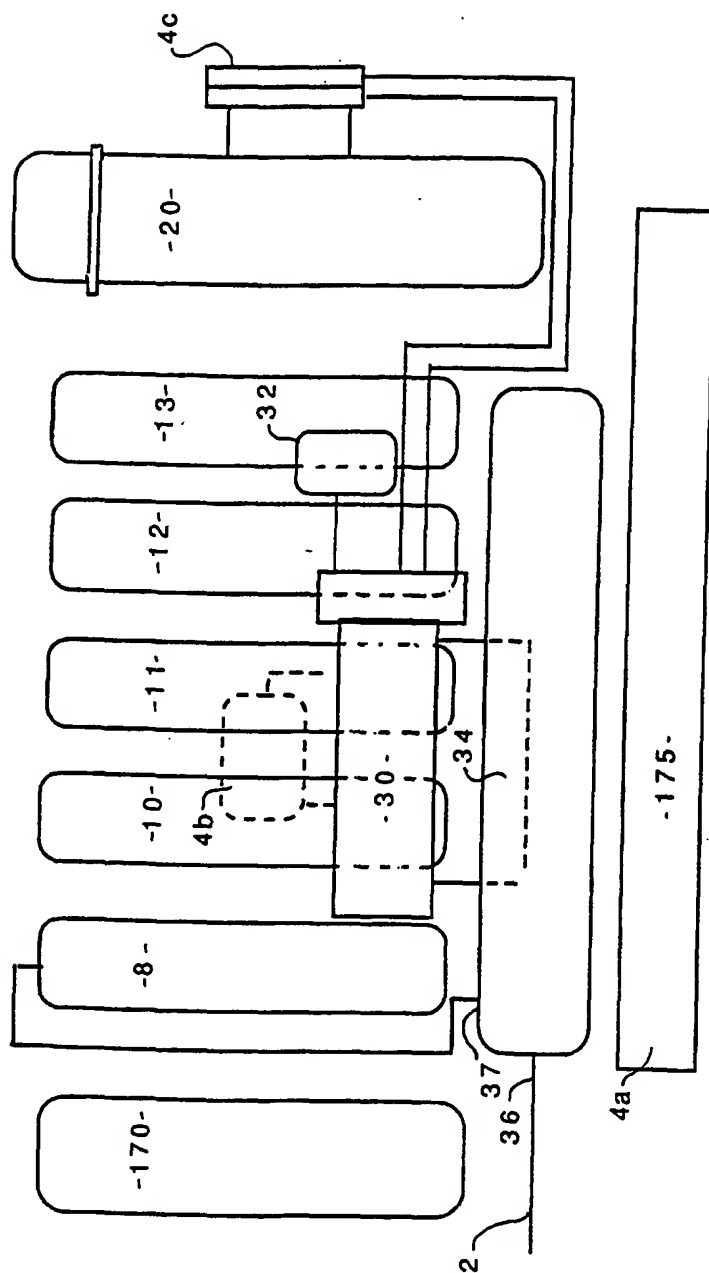


FIGURE 2

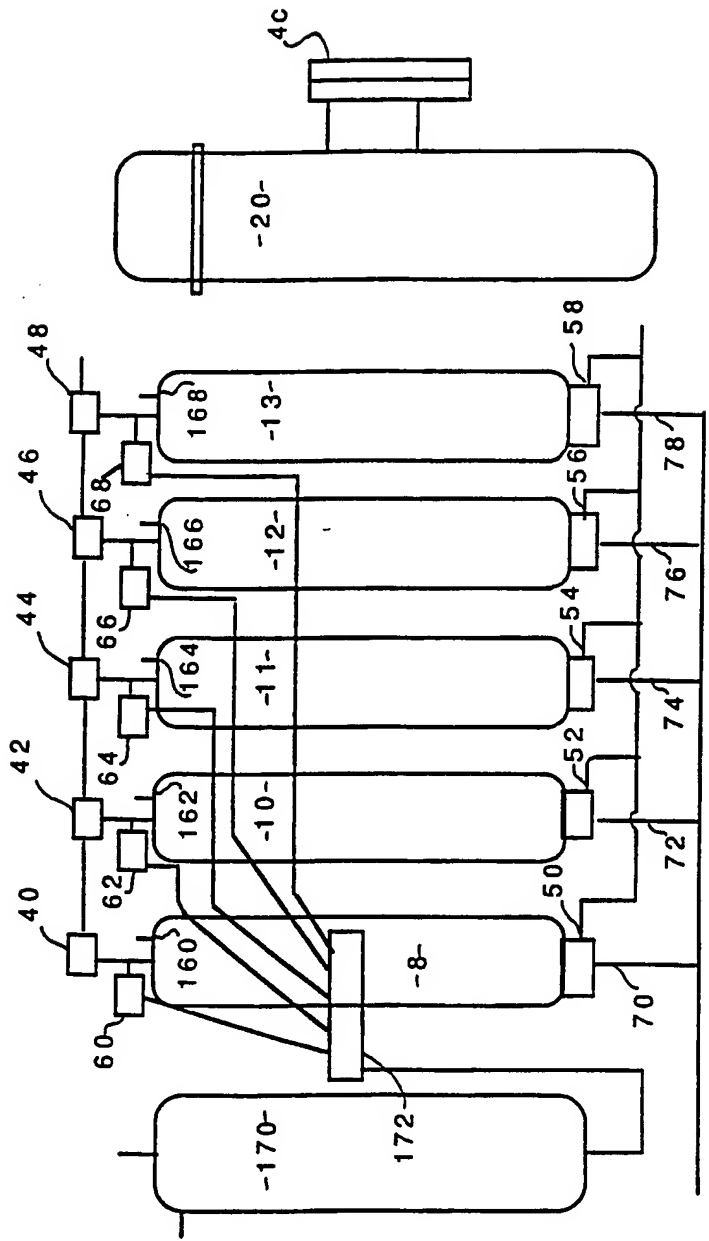


FIGURE 3

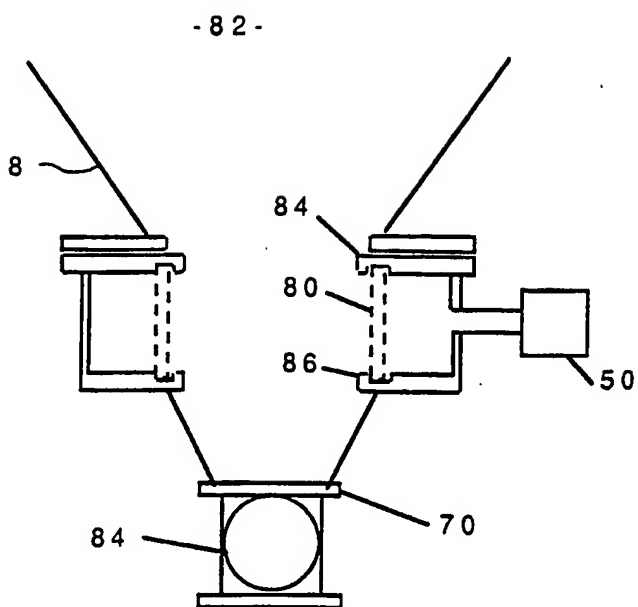


FIGURE 4

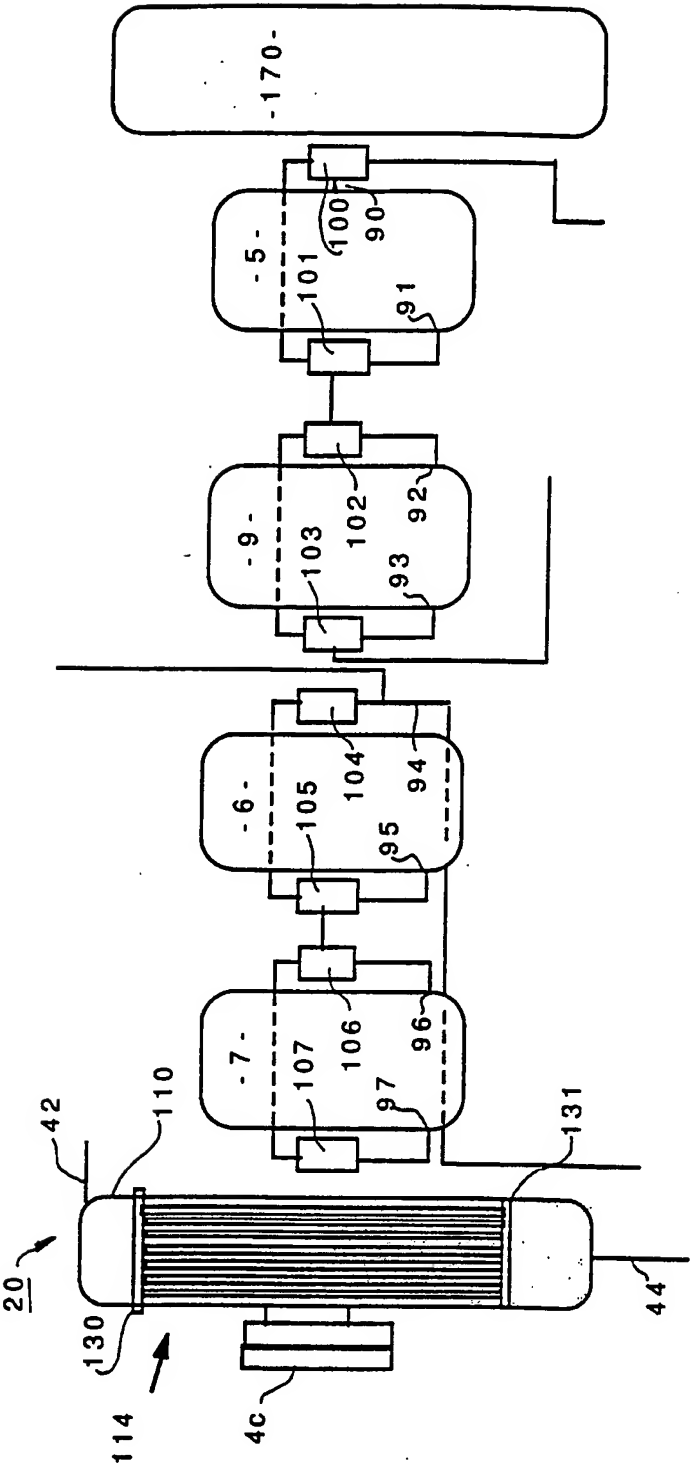


FIGURE 5

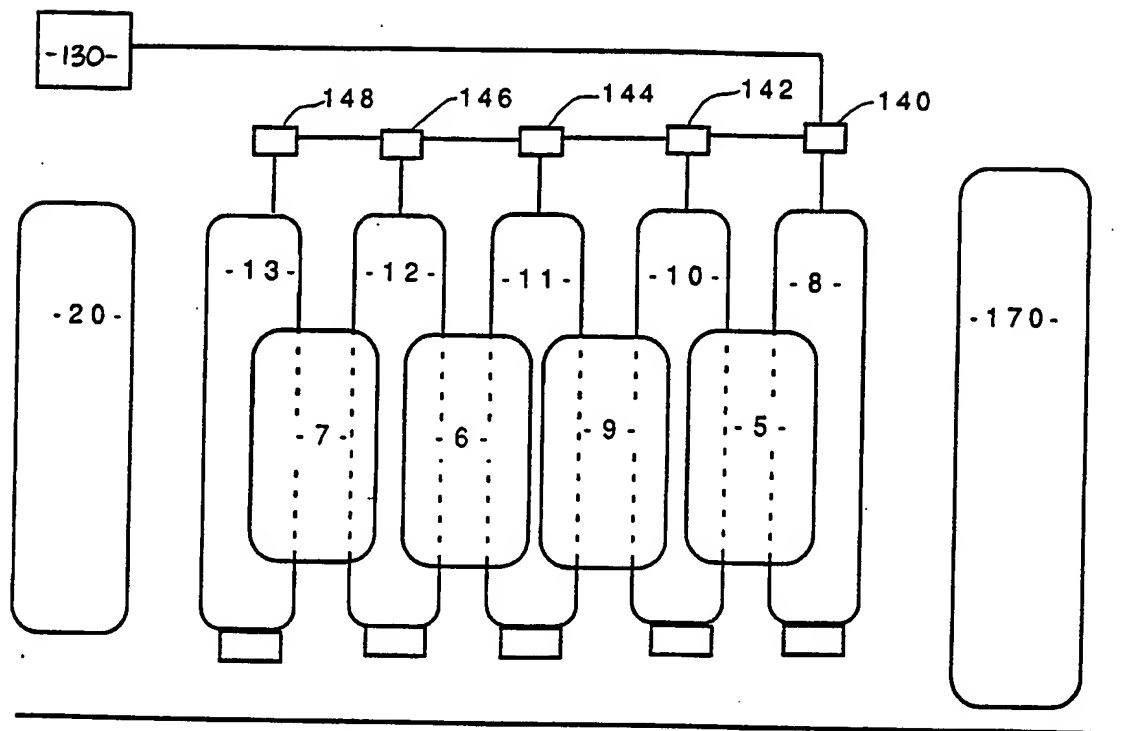


FIGURE 6

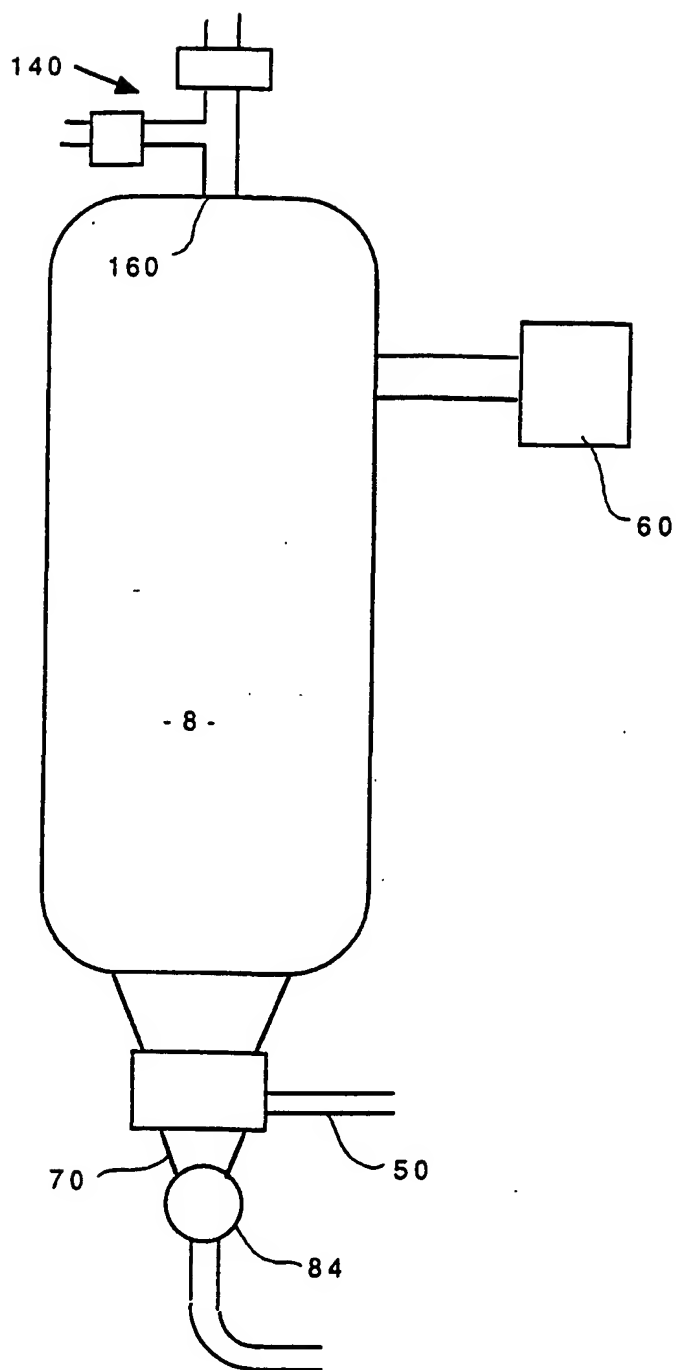


FIGURE 7

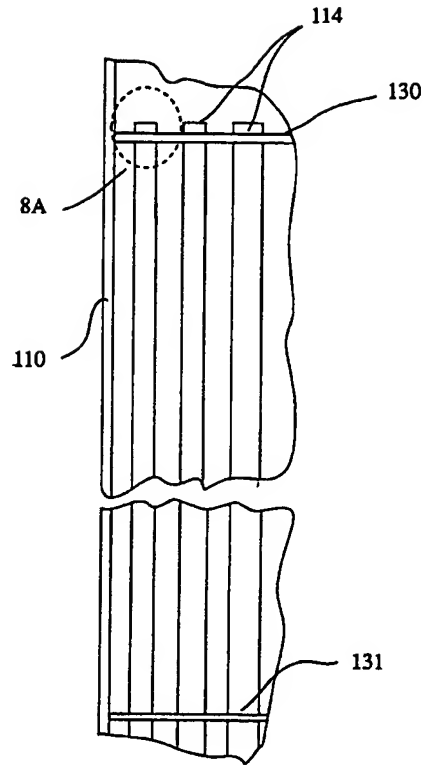


FIG. 8

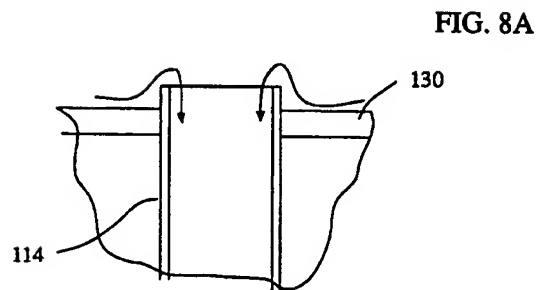



FIG. 8A

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁶ C10M 175/00 According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC C10M 175/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT:					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.			
X	SU, A, 418517 (BORODYANSKII at al.) 19 August 1974 See whole abstract	1, 5			
A	US, A, 4498992 (GARRETT) 12 February 1985				
A	DE, A, 4212972 (DEUT AEROSPACE AG) 21 October 1993				
A	DE, A, 4201424 (HOSCHEX GMBH) 22 July 1993				
A	DE, A, 4303783 (AEG TRO TRANSFORMATOREN & SCHALTGERAETE) 11 August 1994				
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. </div>					
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 10%; vertical-align: top; text-align: center;"> "T" "X" "Y" "&" </td> <td style="width: 40%; vertical-align: top;"> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family </td> </tr> </table>			* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family			
Date of the actual completion of the international search 6 June 1995		Date of mailing of the international search report 9 JUNE 1995 (09.06.95)			
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer  J. DEUIS Telephone No. (06) 2832146			

INTERNATIONAL SEARCH REPORT

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	EP, A, 0307716 (TAKANO CORPORATION) 22 March 1989	

INTERNATIONAL SEARCH REPORT**Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)**

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The International application contains multiple inventions because the invention of claims 10-13 are not so linked with those of claims 1-9 as to form a single inventive concept ("unity of invention"). Claims 1-9 define a process and apparatus directed to treating contaminated liquids via filtration, heating, adsorbing (with granular adsorbents) and degasifying. Claims 10-13 is only limited to a apparatus regarding an evaporator/ degasifier means. Consequently, claims 10-13 do not share the characterizing features of claims 1-9. Therefore, claims 10-13 do not share common novel features of claims 1-9.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-9

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4212972	CA JP	1111035 55015464	DE	2830998	EP	7520
US	4498992	CA	1227026				
EP	307716	CN	1032467	JP	1074710		

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

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(54) Title: PROCESS FOR SEPARATING WATER FROM CHEMICAL MIXTURES (57) Abstract The present invention relates to novel compositions of drying agents of superabsorbent polymers, molecular sieves and mixtures thereof and binders of polyurethane foam, polyisocyanurate foam and supports comprising cellulose and a method for separating, drying and/or filtering chemical mixtures. The composition and method of the invention have broad applicability. They may be used for example to remove water from chemical mixtures like refrigerants (e.g., in vehicular refrigeration systems), air (e.g., in vehicular braking systems), natural gas and cleaning solvents (e.g., used in semiconductor manufacture and pipeline cleaning).		

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PROCESS FOR SEPARATING WATER FROM CHEMICAL MIXTURES**Cross Reference to Related Applications**

This application is a continuation-in-part of pending U.S. Patent Application Serial No. 08/967,632 filed November 10, 1997. Priority is claimed from pending
5 Provisional Patent Application Serial No. 60/112,546 filed December 16, 1998. Both of these applications are incorporated herein by this reference.

Field of the Invention

The present invention relates to novel desiccant compositions comprised of certain drying agents and binders and a method for separating, drying and/or filtering
10 chemical mixtures. The composition and method of the invention have broad applicability. They may be used for example to remove water from chemical mixtures like refrigerants (e.g., in vehicular air conditioning systems), air (e.g., in vehicular braking systems), natural gas and cleaning solvents (e.g., in semiconductor manufacture and pipeline cleaning).

Background of the Invention
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A number of methods have been developed in order to separate water from chemical mixtures. The known methods include the use of alkaline earth compounds, carbon molecular sieves, oleum, distillation, and membranes. Many of the known methods are disadvantageous because the processes are inefficient or uneconomical;
20 the drying agents undergo undesirable side reactions and/or adsorbs or absorbs the material being dried (See, U.S.P. 5,347,822).

Drying agents used principally in connection with circulating refrigerants include activated aluminum oxide, silica gels and molecular sieves in solid or granulated form. During use, these materials are abraded by the flow of the cooling
25 liquid and mechanical vibrations and form dust particles. In order to prevent the dust from clogging the valves and conduits of the refrigeration system, a filter must be employed. This costs time (for installation) and money.

The compositions and method of the invention overcome the difficulties associated with the prior art. In particular, we have found that certain of the compositions eliminate the need for a separate filter element.

Summary of the Invention

5 A composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of
10 polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

 A process comprising contacting a chemical mixture comprising water with an
15 effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting
20 of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose

Detailed Description of the Invention

A. The Desiccant Composition

The invention relates to a desiccant composition comprising a drying agent and a binder. Specifically, the invention relates to the following compositions: A composition comprising a drying agent and a binder wherein: (a) said drying agent

comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

In another embodiment, the drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

In yet another embodiment, the drying agent comprises 50 weight percent of a molecular sieve and said binder comprises from 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

1. Drying Agent

For purposes of this invention the following terms have the indicated meanings: "Polymer" means a homopolymer, copolymer (not limited to only two components), or mixtures thereof having a molecular weight of from 1,000,000 to 100,000,000 and preferably from 10,000,000 to 100,000,000 and more preferably from 85,000,000 to 100,000,00 and which are crosslinked sufficiently to impart moisture absorbing or adsorbing properties; "Superabsorbent Polymer" means a Synthetic or Semi-Synthetic (defined below) Polymer that swells, to at least twice its dry volume, with the addition of water at room temperature after standing for up to two hours; Semi-Synthetic means a derivative of a naturally occurring Polymer; and "Synthetic" means a Polymer produced through chemical reaction.

Exemplary Semi-Synthetic Polymers include, without limitation, cellulose ethers, modified starches, starch derivatives, natural gum derivatives, and mixtures thereof. Illustrative Synthetic Polymers include, without limitation, polymers, related polymers, and polymer salts of acrylamide, acrylic acid, ethylene oxide, methacrylic

acid, polyethyleneimine, polyvinyl alcohol, polyvinyl pyrrolidone, and mixtures thereof. For purposes of this invention "related polymer" means that the polymer repeat unit, or a branch thereof, is extended by carbon atoms, preferably from one to four carbon atoms. For example, a related polymer of acrylic acid is one in which the vinyl group is extended by one carbon to form an allyl group.

Synthetic Polymers are preferred. Polyacrylic acid and its salts are more preferred and sodium polyacrylate (such as SXM70 and SXM77 from Stockhausen of Greensboro, North Carolina) and potassium polyacrylate are most preferred.

Any molecular sieve may be used in the composition of the invention. These materials are commercially available from for example UOP of Des Plaines, Illinois and Grace Corporation of Baltimore, Maryland. They may also be prepared by methods well known in the art. Suitable molecular sieves include without limitation: Type A, Type B, Type L, Type X, Type Y and mixtures thereof. In the practice of this invention Type A is preferred. For refrigeration applications molecular sieves of 3 – 4 Angstroms are preferred such as XH6, XH7, XH9 and XH11 from UOP.

Multiple drying agents may be used in the compositions and method of the invention. Besides Superabsorbent Polymers and molecular sieves, other known drying agents can optionally be employed in the compositions of the invention. They include without limitation activated alumina, activated carbon, silica gel and mixtures thereof. When multiple drying agents are used they may be used in any ratio that is from 1 to 99 to 99 to 1.

The selection of drying agent(s) including type and form will depend on the process (including materials and equipment) that produces the chemical mixture or in which the chemical mixture is being used. The shape and hardness of the drying agent should be chosen to withstand the rigors of the system in which it is used and to avoid entrainment in the equipment, plugging openings and conduits. The drying agent may be a powder, fine particles, fibers, or a shaped piece or pieces. We have found that a 50/50 mixture of superabsorbent polymer and molecular sieve (with 50 weight percent binder) provides superior capacity and drying ability than either drying agent

alone in a process for separating water from halogenated hydrocarbons, for example a refrigerant such as R-134a.

2. Binder

Any material capable of supporting the drying agent (including water
5 absorbed/adsorbed in the drying agent) when may be used in the invention. Suitable
binder materials include, without limitation, organic plastic binders such as
isocyanate-based polymers, phenolic resins, aliphatic epoxy resins, silicone, polyvinyl
alcohol resins, polyphenylene sulfide, poly(ether ketone), polyether sulfone, supports
comprising cellulose and mixtures thereof. Polyurethane foam, polyisocyanurate foam
10 and supports comprising cellulose are preferred. These materials are known in the art
and can be purchased commercially or prepared by known methods. See, for example,
U.S.P.'s 4,986,930, 4,655,757, 4,340,556, 4,596,567, 2,882,244, 2,950,952, 2,882,243
and 3,130,007 the disclosures of which are hereby incorporated by reference.

It is important to select a binder material that can be processed at a
15 temperature that does not destroy the drying agent. In the case of thermoplastic
binders, the processing temperature should be less than 300°C, preferably less than
250°C.

The desiccant compositions of the invention can be prepared by adding the
drying agent as one of the components in the process (e.g, polymerization) used to
20 prepare the binder. When a polyurethane foam or polyisocyanurate foam binder is
used, the desiccant composition can be prepared by adding the drying agent with the
other foam ingredients from the same or a different mix head and foaming the
mixture. If a preblend of the foam ingredients is used, the drying agent can be added
to the "A" and/or "B side" of the preblend. Preferably it is added to the "B side".

25 When cellulose is the binder, preferably, the desiccant composition has a
lamine structure (i.e, layered e.g., binder/drying agent/binder etc.) Desiccant
compositions which utilize a support comprising cellulose may be prepared by
following the procedure outlined in European Patent Application 0 359 615.

The amount of drying agent and binder utilized in the desiccant composition is application dependent. Each should be used in "effective amounts" where this term means that amount of drying agent and optionally binder necessary to achieve a desired degree of dryness, separation and/or filtering and that amount of binder
 5 necessary to support the drying agent. This amount is readily determined by consideration of the amount of water sought to be separated, the flow rate of the chemical mixture, and the adsorptive or absorptive characteristics of the drying agent and binder. Generally, the desiccant compositions have the compositions disclosed in Table I below. The numerical ranges are understood to be prefaced by "about."

10

Table I

Desiccant Composition	Range (wt.%)	Preferred Range (wt.%)	More Preferred Range (wt.%)	Most Preferred Range (wt.%)
Drying agent	10 – 80	20 – 75	30 – 70	40 – 65
Binder	90 – 20	80 – 25	70 – 30	60 – 35

The requisite initial dryness of the drying agent will depend on such factors as the amount of water in the chemical mixture to be dried, the amount of drying agent used, and the equilibrium concentration of water in the drying agent when it is in
 15 contact with the chemical mixture at its final, or desired, water content. Preferably, the drying agent is dried to the greatest extent possible prior to. The temperature at which the drying agent is dried should be high enough to remove water without degrading the drying agent. In the case of molecular sieves this drying is conducted generally in a vacuum desiccator at temperatures up to 300°C. In the case of
 20 Superabsorbent Polymers the drying is conducted again in a vacuum desiccator but at temperatures between 100 and 200°C. As the drying agent loses water, its weight decreases until it reaches a constant weight. At this point, the drying agent has been dried to the greatest extent possible at that particular temperature.

If the application requires that all but 10 ppm or less of water be removed from the chemical mixture, it may be necessary to use an essentially anhydrous Water-Soluble Polymer. For purposes of this invention, "essentially anhydrous" means that the drying agent contains less than 1 weight percent water.

5 B. Process

The amount of desiccant composition utilized will depend again on the application. An effective amount of the desiccant composition should be used where this term means an amount necessary to achieve a desired degree of dryness, separation and/or filtering. This amount is readily determined by consideration of the amount of water sought to be separated, the flow rate of the chemical mixture, and the adsorptive or absorptive characteristics of the drying agent and binder. Generally, the desiccant composition is used in an amount of from 3 to 700 percent, preferably from 100 to 700 percent and most preferably from 200 to 700 percent based upon the amount of water to be removed.

15 In another embodiment, the invention relates to a process comprising: contacting a chemical mixture comprising water with a drying effective amount of a desiccant composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

For purposes of this invention, a chemical mixture is a liquid, gaseous or partially gaseous mixture of water and at least one inorganic material, organic material, or mixtures thereof. Illustrative inorganic materials include, without limitation, air, hydrogen, hydrogen chloride, sulfur dioxide, sulfur trioxide, carbon

monoxide, carbon dioxide, boron trifluoride, uranium hexafluoride, sulfur hexafluoride, arsenic pentafluoride, halide salts, nitric acid, sulfuric acid, chlorine, metal ions, non-aqueous inorganic solvents, and mixtures thereof. Exemplary organic materials include, without limitation, alcohols such as methanol, ethanol and
5 propanol, ketones including acetone, and aromatics including benzene, toluene and naphthalene, hydrocarbons, including gaseous hydrocarbons such as methane, ethane, propane and butane; and halogenated hydrocarbons such as chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons, chlorocarbons, hydrochlorocarbons, hydrofluoroethers, fluoroethers, and mixtures thereof, including
10 without limitation difluoromethane, trifluoroethane, tetrafluoroethane, pentafluoroethane, pentafluoropropane and the like.

The process of the invention may be carried out in any suitable vessel. In the process of the invention, the chemical mixture is contacted with the desiccant composition for from 1 to 24 hours, preferably from 1 to 6 hours and most preferably
15 from 1 to 4 hours.

In a particular application of the process embodiment, the desiccant composition is utilized in a refrigeration system such as a car air conditioning system to absorb water from the refrigerant. In this application, the process comprises cycling a refrigerant in a system wherein the refrigerant is condensed and thereafter
20 evaporated, said system comprising an effective amount of a composition comprising an drying agent and a binder wherein said drying agent comprises an effective amount of a material selected from the group consisting of superabsorbent polymer, molecular sieve and mixtures thereof and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam and
25 polyisocyanurate foam and a support comprising cellulose.

In this application, the desiccant composition may comprise the core of a drier. A drier core which utilizes a drying agent of the invention with a polyurethane foam or polyisocyanurate foam binder, may be prepared by adding the drying agent to a foam formulation in the manner discussed above and foaming the composition in a
30 container, the resulting desiccant composition would comprise the core and the

container the drier. A drier core which utilizes a drying agent of the invention and a support comprising cellulose as the binder, can be prepared by adding the drying agent to the cellulose binder as discussed above and rolling or stacking the resulting composition in a container. The desiccant composition would once again comprise the
5 core and the container the drier. This drier core would be fixed in the refrigeration system in the circulation path by means known in the art.

Applicants have discovered that a desiccant compositions comprising a mixture of a Superabsorbent Polymer and molecular sieve and a polyurethane or polyisocyanurate foam binder are particularly useful in this process embodiment
10 especially at loadings of 50 weight percent drying agent (50:50 ratio of drying agents) and 50 weight percent foam. This composition exhibits several advantages over prior art materials including greater capacity and drying ability, smaller volume and elimination of a separate filter element.

In another application of the process of the invention, the invention can be
15 used to absorb water from spent cleaning solvent such as that used in semiconductor manufacture or natural gas or other pipeline cleaning. The process would comprise exposing a solvent comprising water to a desiccant composition of the invention. This could be done after the solvent was recovered as a separate step or during the cleaning process itself. In the latter application, the desiccant composition would be fixed, for
20 example, to the inside of a pipeline and the solvent in the course of passing through the pipeline would pass through the desiccant and water would be removed from the solvent. In still another application of the process of the invention, the invention can be used to absorb water from air such as for example in air brake applications.

In all embodiments, the performance of the drying agent may be improved by
25 periodically regenerating the drying agent to release the water separated from the chemical mixture. Regeneration may be accomplished by any convenient means, such as by heating the drying agent to a temperature suitable to release water from the drying agent.

The amount of water removed by the Superabsorbent Polymer must be monitored in order to maintain its mechanical integrity. If the Superabsorbent Polymer is in solid form, allowing the amount of water separated from the chemical mixture by the Superabsorbent Polymer to reach a level at which it turns from a solid
5 into a gel or liquid may be disadvantageous. The amount of water at which this phase change occurs will vary depending on the Superabsorbent Polymer used but is readily determined by routine experimentation. Preferably, the Superabsorbent Polymer is used to a point just below the point at which a phase change occurs. Water separation may be monitored by any convenient means as for example, measuring the amount of
10 water in the chemical mixtures. Further, if one or more other chemicals in the chemical mixture forms a gel or solid with the Superabsorbent Polymer, the water required for the solid to liquid phase change may be altered.

If very low levels of water are desired in the chemical mixture, that mixture may be treated sequentially with more than one drying agent bed to reach the desired
15 level. We have discovered the use of a sodium polyacrylate polymer bed followed by a molecular sieve bed is particularly effective. Alternatively, the process of the invention may be used in conjunction with other well known drying methods.

The invention will be clarified further by a consideration of the following examples, which are purely exemplary.

20 Examples

Example 1

This example demonstrates the preparation of a desiccant composition comprising polyurethane foam and a superabsorbent polymer. The isocyanate or A component of the mixture used was Mondur 2OS available from Bayer Corporation.
25 The formulation of the B component of the mixture was as follows:

50 parts VORANOL-490 (polyol available from Dow Chemical Co.)
50 parts VORANOL-391 (polyol available from Dow Chemical Co.)
2.5 parts L-6164 (surfactant available from Goldschmidt Chemical Co.)
3.2 parts POLYCAT 41 (catalyst available from Air Products and Chemicals)
5 53 parts HCFC-141b (blowing agent available from AlliedSignal Inc.).

The A and B side were mixed together and sodium polyacrylate (constituting 43 weight percent of the entire mixture) was added to the mixture and quickly stirred. The whole mass was then poured into a 150 cc Teflon vessel. The vessel was capped and the foam allowed to rise. The vessel was equipped with ports on both ends so that
10 gaseous refrigerant could be passed through it.

Example 2

A sample of R-134a containing 578 ppm water was passed through the vessel described in Example 1 above which contained 27 grams of the potassium salt of polyacrylic acid and foam (The potassium salt of polyacrylic acid comprised 43% of
15 the composition). The moisture content on exiting the vessel was measured using a Karl Fischer coulometer and found to be 25 ppm.

Example 3

The experiment of Example 2 is repeated except that R-134a containing 1114 ppm water was passed through a different vessel containing 51.3 grams of the
20 desiccant composition (containing 43% of the potassium salt of polyacrylic acid). The moisture content on exiting the vessel was 23 ppm.

Example 4

A desiccant composition was prepared as in Example 1 except that the sodium polyacrylate constituted 70 weight percent of a 30 gram sample. Wet nitrogen was
25 passed through the vessel until the desiccant composition had absorbed 20% of its dry weight in water. R-134a was then passed through the vessel very slowly. The exiting R-134a had a moisture content of 180 ppm. This example demonstrates the superior capacity of the desiccant composition in that even after having absorbed 20% of its

dry weight in water, the moisture concentration is far below that reported in the 1994 ASHRAE Handbook for molecular sieve (800 ppm at 16% of its dry weight in water). (I do not understand this)

Example 5

5 A desiccant composition is prepared as in Example 1 except that the polyol used is polybutylene oxide and the sodium polyacrylate constitutes 60 weight percent of a 30 gram sample. Wet nitrogen is passed through the vessel until the desiccant composition absorbs 20% of its dry weight in water. R-134a is passed through the vessel very slowly. The exiting R-134a has a moisture content of 180 ppm.

10 Example 6

 A desiccant composition is prepared as in Example 1 except that the polyol used is polypropylene oxide and the sodium polyacrylate is 60 weight percent of a 30 gram sample. R-134a is passed through the vessel very slowly. The exiting R-134a has a moisture content of 180 ppm.

15 Example 7

 Sodium polyacrylate deposited on cellulosic material was obtained from Gelok International. The material's tradename is 9525 s/s. A strip that measured 16 in. x 2 in. was rolled to fit into a stainless steel cylinder that was 11.5 in. tall with a diameter of 1.5 in. The cylinder was initially open at both ends. Two ends with tube
20 connection were then bolted on to the cylinder. This fixture was then connected to an apparatus comprising a pump, a supply cylinder of dry R-134a, a flow meter and a loop that bypassed the fixture. The loop contained Celite that was saturated with water. A Panometrics MIS2 probe for measuring the moisture in liquid refrigerants was attached in line with the fixture. The apparatus, with the refrigerant supply
25 cylinder valves closed, was evacuated. The valves were then opened and liquid refrigerant fed to the pump and the pump turned on. In order to wet the refrigerant, the fixture was closed off and the refrigerant fed through the bypass loop. The bypass was then closed and the fixture opened. The reading on the probe was initially off

scale indicating a very high moisture level. After a few minutes the probe registered 380 ppm. After three hours the concentration of water in the R-134a was measured to be 100 ppm.

Example 8

5 A rigid, open-celled foam was blown into a cylinder that was 4 in. long and 1.5 in. in diameter. The foam formulation contained a mixture of sodium polyacrylate and molecular sieve (7.25 grams each). The cylinder was initially open at both ends. Two ends with tube connection were then bolted on to the cylinder. This fixture was then connected to an apparatus comprising a pump, a supply cylinder of dry R-134a, a
10 flow meter and a loop that bypassed the fixture. The loop contained Celite that was saturated with water. A Panometrics MIS2 probe for measuring the moisture in liquid refrigerants was attached in line with the fixture. The apparatus, with the refrigerant supply cylinder valves closed, was evacuated. The valves were then opened and liquid refrigerant fed to the pump and the pump turned on. In order to wet the refrigerant,
15 the fixture was closed off and the refrigerant fed through the bypass loop. The bypass was then closed and the fixture opened. The reading on the probe was initially off scale indicating a very high moisture level. After 6 minutes the probe registered 528 ppm. After 50 minutes the concentration of water in the R-134a was measured to be 86 ppm.

20

What is claimed is:

1. A composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.
2. The composition of claim 1 (a).
3. The composition of claim 1 (b).
4. The composition of claim 1 (c).
5. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.
6. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 20 to 75 weight percent and said binder is present in an amount of from 25 to 80 weight percent.
7. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 30 to 70 weight percent and said binder is present in an amount of from 30 to 70 weight percent.
8. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 40 to 65 weight percent and said binder is present in an amount of from 35 to 60 weight percent.

9. The composition of claim 1 (b) wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.
- 5 10. The composition of claim 1 (b) wherein said drying agent comprises 50 weight percent of a molecular sieve and said binder comprises 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.
11. The composition of claim 1 (a) wherein said support has a laminate structure.
- 10 12. The composition of claim 1 (b) wherein said binder is polyurethane foam.
13. The composition of claim 1 (b) wherein said binder is polyisocyanurate foam.
14. The composition of claim 1 (c) wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.
15. The composition of claim 1 (c) wherein said binder comprises polyurethane foam.
- 15 16. The composition of claim 1 (c) wherein said binder comprises polyisocyanurate foam.
17. The composition of claim 1 (c) wherein said binder comprises a support comprising cellulose.
18. The composition of claim 17 wherein said support has a laminate structure.
- 20 19. A process comprising contacting a chemical mixture comprising water with an effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said
25 binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying

agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

- 5
20. A process comprising contacting a chemical mixture comprising water and a halogenated hydrocarbon with an effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.
- 10
21. The process of claim 20 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose.
- 15
22. The process of claim 20 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.
- 20
23. The process of claim 20 wherein said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.
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24. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.
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25. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 20 to 75 weight percent and said binder is present in an amount of from 25 to 80 weight percent.
26. The process of claim 21 or 23 wherein said drying agent is present in an amount
5 of from 30 to 70 weight percent and said binder is present in an amount of from 30 to 70 weight percent.
27. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 40 to 65 weight percent and said binder is present in an amount of from 35 to 60 weight percent.
- 10 28. The process of claim 22 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.
- 15 29. The process of claim 22 wherein said drying agent comprises 50 weight percent of a molecular sieve and said binder comprises 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.
30. The process of claim 22 wherein said binder comprises polyurethane foam.
31. The process of claim 22 wherein said binder comprises polyisocyanurate foam.
- 20 32. The process of claim 21 wherein said binder has a laminate structure.
33. The process of claim 23 wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.
34. The process of claim 23 wherein said binder comprises a polyurethane foam.
35. The process of claim 23 wherein said binder comprises a polyisocyanurate foam.

36. The process of claim 23 wherein said binder comprises a support comprising cellulose.
37. The process of claim 36 wherein said support has a laminate structure.
38. The process of claim 20 wherein said halogenated hydrocarbon comprises a hydrofluorocarbon.
39. The process of claim 38 wherein said hydrofluorocarbon comprises difluoromethane.
40. The process of claim 20 wherein said composition further comprises at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.
41. The composition of claim 1 wherein said composition further comprises at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.
42. The process of claim 19 wherein said chemical mixture comprises air.
43. A drier core comprising an effective amount of a composition comprising a drying agent and a binder wherein said drying agent comprises an effective amount of a material selected from the group consisting of superabsorbent polymer, molecular sieve and mixtures thereof and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.
44. The drier core of claim 43 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.
45. The drier core of claim 43 wherein said drying agent comprises superabsorbent polymer.

46. The drier core of claim 43 wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.
47. The drier core of claim 43 wherein said drying agent comprises molecular sieve.
48. The drier core of claim 43 wherein said drying agent comprises a mixture of
5 superabsorbent polymer and molecular sieve.
49. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises polyurethane foam.
50. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises polyisocyanurate foam.
- 10 51. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises a support comprising cellulose.
52. The drier core of claim 43 wherein the drying agent further at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.
- 15 53. A process comprising the steps of cycling a refrigerant in a system wherein the refrigerant is condensed and thereafter evaporated, the system having therein a drying effective amount of the composition of claim 1.